

## DETERMINING POLYMERIC GLASS TRANSITIONS USING THERMOGRAVIMETRIC ANALYSIS

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### ABSTRACT

Thermogravimetric analysis is typically employed to study degradation and curing processes. The work presented here will show that thermogravimetry (TG) can also be used to probe other types of thermal processes. In particular, TG can be used to determine glass transitions  $T_g$  in certain polymers. A premise of the technique is that low molecular weight species can be imbedded into a polymer sample. Upon heating, major gas evolution will take place in the glass transition region and such gas evolution can be utilized as an indicator of  $T_g$ . This technique is particularly beneficial for determining  $T_g$  values of semicrystalline polymers without major modifications of crystallinity. To demonstrate the concept, studies were carried out in two phases. Phase one looked at well characterized amorphous polymers using several solvents to show that the technique does indeed work. In phase two it was established that glass transitions of semicrystalline polymers could be detected.

### INTRODUCTION

During the course of research, a novel perspective of fundamental concepts frequently leads to the development of new characterization techniques. For instance, while investigating the thermal degradation of novel isomers of polyvinylidene chloride (PVDC), the principles on which the present technique is based were demonstrated. On heating in a thermogravimetric analyzer, it appeared that, unlike the usual head to tail (h-t) PVDC, which has one major weight loss transition at approximately 200°C, the isomer under investigation, head to head (h-h) PVDC, had two transitions, see Fig. 1a. A small transition had an approximate onset at 130°C, and there was a major transition starting at 315°C. In an effort to determine the source of the secondary transition at 130°C, mass spectrometry was employed in conjunction with thermogravimetric analysis (TG-MS). Such a technique not only allows monitoring of thermal degradation via weight loss associated with evolution, but allows identification of low molecular weight (LMW) species as evolution occurs. The results of this study revealed that only chloroform was evolved during the lower transition (see Fig. 1b). No

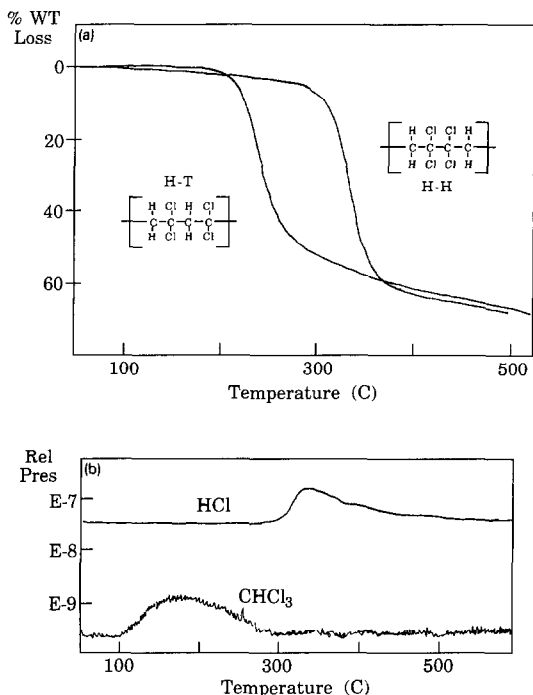


Fig. 1. Weight loss curves for h-t and h-h PVDC (a) and mass spectrum (in mass vs. time mode) of decomposition of h-h PVDC (b).

logical mechanism could be developed which might explain production of chloroform upon thermal degradation; however, it was known that chloroform was used during the purification procedures following synthesis.

To remove residual chlorine, the polymer was extracted with chloroform for several days in a Soxhlet extractor. After extraction, the polymer was dried under vacuum for 36 h at 40°C. This procedure was believed to be sufficient to remove residual chloroform from the sample. Fortuitously, this assumption was incorrect.

Of special note is the observation that the evolution of chloroform, as monitored by TG-MS did not occur until the sample temperature was above 100°C; a full 40°C above the boiling point of chloroform. Taking into consideration sample size and heating rate, a 40°C lag in evolution is too great to be explained by diffusion alone. Before exploring other possible explanations a brief review of the thermal behavior of polymers may prove useful.

Thermoplastics can be classified into one of two groups, amorphous and semicrystalline. Semicrystalline polymers have been described as two-phase systems; crystalline domains in an amorphous matrix. Associated with each phase is a major thermal transition. As in smaller molecules, the crystalline transition is associated with melting. Not studied as often in smaller

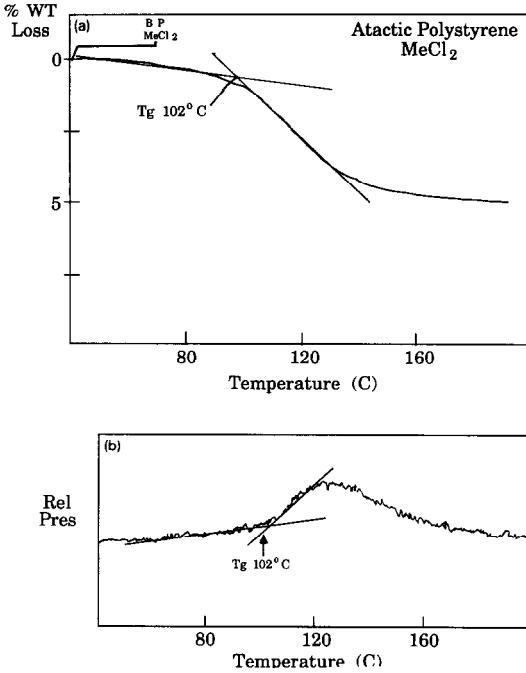


Fig. 2.  $T_g$  calculation for a-polystyrene using (a) TG data and (b) ms data.

molecules is the major amorphous transition, the glass transition temperature  $T_g$ . On heating through  $T_g$ , amorphous polymer transforms from a brittle to a ductile material; thermal energy has been introduced which allows gross movement of large chain segments.

Those of us who use differential scanning calorimetry (DSC) to determine polymer glass transitions are familiar with the phenomena of solvent evolution producing an endothermic peak while passing through this transition region. To this author's knowledge, no one has realized the utility of this effect to investigate glass transitions in semicrystalline polymers. The temperature at which  $T_g$  is observed in semicrystalline polymers is reportedly related to the amount, type and domain size of the crystalline component, and it is of particular interest to be able to determine the  $T_g$  of a semicrystalline polymer in an unperturbed crystalline form. The subtleness of  $T_g$  in highly crystalline polymers makes determination of  $T_g$  difficult if not impossible by techniques such as differential scanning calorimetry. Many times, sample preparation techniques such as solvent or thermal quenching have been employed to inhibit crystallization. With significantly higher percentages of amorphous material, a  $T_g$  for a quenched polymer can usually be determined. Unfortunately,  $T_g$  determined by such methods could be lower than that present in the amorphous phase of a semicrystalline sample. Furthermore, some polymers, such as h-h PVDC, have such a high melting point that neither thermal nor solvent preparation techniques can be utilized

to suppress crystallinity sufficiently to allow any  $T_g$  to be detected by DSC. In such cases, we believe that the presented technique is an excellent recourse for determining glass transitions.

## EXPERIMENTAL

### *Technique*

The basic assumption employed by this technique is that low molecular weight species can be trapped or "frozen in" a polymer sample at temperatures above the LMW species boiling point, but below the  $T_g$  of the polymer. Significant evolution of LMW species occurs only after heating through the glass transition temperature of the polymer. To test the validity of this statement and the utility of this technique, two series of experiments were performed on several polymer-LMW species systems. Phase one involved developing and verifying the technique using amorphous polymers. Because species polarity plays a major role in molecular interaction, it is important to determine if LMW species polarity has any effect on the detected  $T_g$ . The second phase of the work involved further developing the technique and demonstrating that the  $T_g$ 's of semicrystalline polymers can be determined.

In phase one the main concerns revolved around producing evidence to substantiate the stated basic assumption, little concern was given to morphological modification. A simple, straightforward method was used to introduce LMW species into amorphous polymers. Polymers were dissolved in solvents with boiling points above room temperature, but sufficiently below the  $T_g$  of the polymer. Once in solution, solvent was evaporated from the samples. After a significant portion of solvent had been removed via air evaporation, the samples were placed under vacuum at room temperature for 48 h. It was hoped that approximately 5% by weight of solvent would remain after this procedure.

### *Procedure*

The polymers used were atactic polystyrene [PS(a)] ( $T_g = 100^\circ\text{C}$  by DSC) and chlorinated poly(vinyl chloride) (CPVC) ( $T_g = 126^\circ\text{C}$ ) [1]. Two samples of PS(a) were prepared; one containing methylene chloride (b.p. =  $40^\circ\text{C}$ ) and one containing tetrahydrofuran (b.p. =  $66^\circ\text{C}$ ). A sample of CPVC containing tetrahydrofuran was also prepared.

Samples used during phase two were prepared by different means from those in phase one. The goal of this portion of the study was to investigate the values  $T_g$  of semicrystalline polymers without destroying crystalline morphology; LMW species which are nonsolvents for crystalline domains were employed. Head to head PVDC ( $T_g$  not known) and crystallizable

isotactic polystyrene [PS(i)] ( $T_g = 95^\circ\text{C}$  by DSC), were investigated during this phase.

Nonsolvents were introduced into the polymer by one of two routes. As described previously, chloroform (b.p. =  $61^\circ\text{C}$ ) was imbibed into PVDC using a Soxhlet extractor for 48 h. An alternative method consisted of placing PS(i) in an atmosphere containing high concentrations of nonsolvent vapors (hexane; b.p. =  $69^\circ\text{C}$ ) for 24 h. After these procedures, both samples were placed under vacuum for 48 h at  $40^\circ\text{C}$ . It was hoped that samples prepared in this manner would permit LMW species to penetrate deep into the amorphous regions.

Once prepared, each sample was examined by TG-MS. The TG analyzer used was a Perkin-Elmer TGS-2 with System 4 temperature programmer and TADS data station. A Dycor M200 Gas Analyzer equipped with a capillary sampling system was used in conjunction with TG. The end of the capillary was placed just above the sample's surface. As mentioned, such a system allows not only monitoring of the extent of weight loss due to gas/solvent vapor evolution, but also identification of off-gassed species. Using sample sizes ranging from 5 to 15 milligrams, experiments were conducted at a heating rate of  $10^\circ\text{C min}^{-1}$  over a range from 30 to  $200^\circ\text{C}$ . If this type of instrumentation is not available, a TG instrument will suffice for the  $T_g$  calculations.

Finally, before discussing any results, a statement on technique limitations should be made. Most TG units are not equipped for sub-ambient temperatures, therefore polymers investigated must have potentially high  $T_g$ 's ( $T_g > 70^\circ\text{C}$ ). In addition, the LMW species should have a boiling point below the  $T_g$  in order that solvent evolution at  $T_g$  will not be masked. Further, the LMW species should not interact with the crystalline phase.

## RESULTS AND DISCUSSION

The glass transition as determined by DSC is somewhat dependent on definition and how intercept lines are constructed. Unfortunately, the same type of problem exists here. Because evolution has been described as taking place as one heats through  $T_g$ , then the glass transition is considered to be the onset of weight loss as monitored by TG. By constructing tangent lines through the initial baseline and the weight loss portion, an onset or glass transition may be calculated, see Figs. 2a and b. Care needs to be taken to consistently construct all lines in the same manner in order to minimize errors. Development of intensity at a mass number corresponding to the LMW species used also signals the onset of solvent loss. However, the mass spectrometer suffers from mixing problems created by the large volume of the TG sampling chamber. As a result it is not recommended that  $T_g$  values

TABLE 1

Tabulation of data

Polymer	$T_g$ ( $^{\circ}$ C)			Wt. loss (%)	LMW	b.p. ( $^{\circ}$ C)
	DSC	Wt. loss	M.S.			
PS(a)	100	102	102	5	MeCl <sub>2</sub>	40
PS(a)	100	100	100	5	THF	66
CPVC	126	84	102	12	THF	66
PS(i)	95	93	—	0.5	Hexane	69
h-h PVDC	?	128	135	5	CHCl <sub>3</sub>	61

be calculated using MS data, although they have been calculated here for demonstrative purposes; see Figs. 2a and b, and data tabulated in Table 1.

Can a LMW species be trapped in a polymer sample at temperatures significantly above its boiling point? The results from experiments on amorphous samples appear to indicate that this is possible. Significant evolution could not be detected at temperatures 30 $^{\circ}$ C above the boiling point of the respective LMW species. Furthermore, when significant LMW species evolution did occur, the sample temperature was in the approximate range of that reported for the  $T_g$ . Such results strongly support the basic theoretical concepts which are the basis of this technique.

Not all results were as anticipated. A quick review of Table 1 reveals that the measured and reported  $T_g$  values for CPVC do not correlate as well as other examples. This observation can be attributed to one of the major sources of concern with this technique, namely plasticization. The temperature at which the glass transition of a particular polymer sample is detected can be greatly affected by introducing molecules which are miscible with the amorphous phase and have drastically different  $T_g$  values from the polymer. Such plasticization is additive; that is  $T_g$  varies with composition, higher concentrations of LMW species lead to lower measured  $T_g$  values.

There are several ways to correct for the effects of plasticization described here. One approach involves performing TG on several samples with varying concentrations of LMW species. Plotting onset as a function of total weight loss, and in this case a rather long extrapolation to zero weight loss, yields an unplasticized  $T_g$  in good agreement with previously determined DSC value for  $T_g$ , see Fig. 3. If a  $T_g$  of the LMW species is available the unplasticized  $T_g$  can be calculated using a variation of an equation developed by Beuche [2].

From the limited experiments performed, it would appear that LMW species/polymer interaction has a variety of effects on evolution temperature. Results depend on both the polarity of the LMW species and the polymer. In the case of polystyrene (both iso- and atactic) LMW species of varying polarity all evolved at approximately the same temperature. This

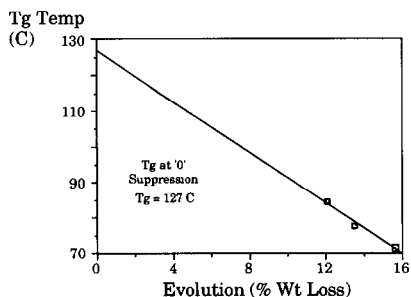


Fig. 3. Correction plot for  $T_g$  suppression for CPVC.

even includes hexane which is not a solvent for either amorphous or crystalline polystyrene. These results indicate that there is relatively little interaction between polystyrene and LMW species. Conversely, a comparison of amorphous systems where THF was used, demonstrates how drastic plasticization effects can be. Little suppression is indicated in the polystyrene sample where 5% weight loss was detected. On the other hand, a weight loss of 12% corresponds to a 44°C suppression in the  $T_g$  of CPVC, which is a significantly more polar molecule than PS(a). It would appear that THF interacts more with CPVC than PS(a), which presumably leads to a greater suppression of  $T_g$ .

Phase two dealt with using TG-MS to investigate the values  $T_g$  of semicrystalline polymers. The purpose here was to determine the  $T_g$  values of these polymers without destroying crystallinity. The  $T_g$  of the first system investigated, polystyrene, was known. The results obtained correlate quite well with known values (measured  $T_g$  93°C; known  $T_g$  95°C).

Head to head PVDC was the other polymer investigated. Once precipitated after synthesis, the polymer appears to be insoluble, and X-ray diffraction shows the polymer to be semicrystalline [3]. The only transition seen using DSC is a large exotherm associated with degradation. It becomes quite evident that there is a major problem in characterizing most thermal properties of this polymer.

Using TG, a  $T_g$  of 128°C was determined for h-h PVDC, i.e. some 146° higher than h-t PVDC ( $T_g = -18^\circ\text{C}$ ). Reports in the literature on other vinylidene polymers in the series show similar trends. Polyvinylidene fluoride (PVDF) has a  $T_g$  of 0°C, while that of h-h PVDF was reported to be 135°C [4]. Like PVDC,  $T_g$  values of PVDF isomers are significantly different. Furthermore, the scale of the difference is similar (~135°C). Such evidence supports results reported here quite well. So, in both cases, PS(i) and PVDC, TG does an adequate job of detecting  $T_g$  without destroying crystalline structure.

## CONCLUSIONS

Thermogravimetric analysis is typically thought of as a technique used for studying degradation or curing processes. The work presented here demonstrates the utility of TG in studying other thermal processes. Not only has it been demonstrated that polymeric glass transitions can be determined, but glass transition systems which can only be studied with great difficulty using other techniques were also determined.

Phase 1 yields convincing evidence in support of the basic theory involved in using TG to calculate polymeric  $T_g$  values. Results from all the experiments demonstrated the same trend. That is: significant evolution of LMW species did not occur at temperatures in the proximity of their boiling points but close to the  $T_g$  of the polymer. In cases where significant amounts of LMW species were imbibed into samples, the measured  $T_g$  values were lower than the DSC values. This depression was attributed to plasticization effects. Using a method which extrapolates to zero LMW species, a correction for  $T_g$  depression was performed.

Phase 2 revealed equally interesting results. It was demonstrated that nonsolvent LMW species could be diffused into semicrystalline polymer samples. Furthermore, these LMW species were not evolved until the sample temperature was in the range usually ascribed to  $T_g$ . Finally, TG has been shown to be useful for determining the values  $T_g$  of polymers in cases where normal means failed.

This work is not meant to be a definitive statement on TG for determining polymeric  $T_g$  values. On the contrary, the purpose of this paper is to reveal a new technique for investigating  $T_g$  values, to prove that there is substance to the said technique, and to demonstrate some of its utility for investigating polymeric  $T_g$  values.

## REFERENCES

- 1 S. Angeli, A Dielectric Study of the Polymer Blend Systems: Chlorinated Polyvinyl Chloride with Ethylene-Vinyl Acetate Copolymers Penn State Ph.D. Thesis, 1986.
- 2 F. Bueche, Physical Properties of Polymers, Interscience, New York, 1962.
- 3 M. Farr, An Investigation into the Thermal Properties of Head-to-Head Polyvinylidene Chloride and Copolymers. Penn State M.S. Thesis, 1987.
- 4 M. Modena, et. al., J. Poly. Sci., Poly. Lett. Ed., 10 (1972) 153.