Assessment of Degree of Fusion of Rigid PVC from Inverse Gas Chromatographic Measurements

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SYNOPSIS

Inverse gas chromatography of alkanes has been used to assess the degree of fusion of rigid polyvinyl chloride (PVC) extrudates. The relative degree of fusion is provided by ratios of the retention volumes of the alkane probe molecules in the bulk of the PVC. This method is nonintrusive and can be used to measure degree of fusion quantitatively if a completely fused reference material can be provided. The present analysis involves evaluations of the contributions to the overall retention volume of the alkane probes, resulting from adsorption and from bulk diffusion. The diffusivity of the alkanes was clearly dependent on the processing history of the PVC extrudate. A direct variation was observed between the size of the diffusing molecules and their residence time as adsorbates on the polymer surface. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyvinyl chloride (PVC) ranks among the four major thermoplastics used in high volumes. However, more than in most other thermoplastics, the properties of finished PVC articles are very sensitive to processing history.[1] They depend strongly on the achievement of an adequate level of fusion of the PVC granules, a factor dependent on the thermal history, the applied pressure, and the shear experienced by the polymer as it is processed.

Assessment of the state of fusion of PVC has been the subject of much research. Methods employed for the study of unplasticized PVC include capillary extrusion with very short dies.[2] This popular procedure involves the possibility of changing the degree of fusion during the actual analysis, as well as the serious problem of time-dependent flow phenomena.[3,4] Other approaches also have been followed: Solvent resistance[5] is a widely used go/no-go method that is primarily valuable for quality control purposes. Thermal analysis techniques[6-9] have provided a convenient alternative procedure for estimating the

degree of fusion of rigid PVC, but the method has been found unreliable for compounds that contain appreciable amounts of filler.[10] Fusion levels can be ranked on the basis of the rubbery plateau modulus of samples near 110°C.[11] The method is useful for comparisons, but fails to provide quantitative measures of the degree of fusion. The ideal method would be one which provides an objective, quantitative measure of the degree to which the original grain boundaries of the PVC have been erased.

This article reports the use of inverse gas chromatography (IGC) in a search for the noted ideal method to characterize the level of fusion of PVC compounds. In this application IGC is used to evaluate the tendency of small molecules to diffuse into the bulk polymer in the rubbery temperature region. At temperatures above the T_g of the PVC, that diffusion is directly related to the volume accessible to the diffusing species. Since the incomplete fusion of PVC granules would result in some interparticle voids, it may be assumed that diffusion characteristics would provide a useful measure of the fusion state. Thus, it may be feasible to relate the measurement of accessible volumes, and thus the degree of fusion, from IGC data to process variables, including temperature and shear history. The concept was tested in this work by considering rigid PVC

Table I   Rigid PVC Formulation

Material	Parts
PVC, Esso 566 (66K value)	100
Thiotin stabilizer TM 181	
(Morton Tiokol)	1.5[a]
Ca stearate lubricant	1.0[a]
Processing aid, PMMA, K 120N	
(Rohm and Haas)	1.5[a]
High temp. acrylic lubricant/processing	
aid K 175 (Rohm and Haas)	0.75[a]
Rutile (TiO2) pigment	
(NL Chem 2101)	12[a]

[a] Expressed as parts per 100 parts of host polymer.

samples with different, well-defined process histories.

EXPERIMENTAL

The PVC formulation used was modeled on a conventional window profile compound, described in Table I. This differs from commercial formulations only in the omission of an impact modifier. Extrusion was with a Krauss–Maffei conical twin-screw laboratory machine, at three levels of barrel heat coded low (LT), normal (NT), and high (HT). The medium temperature conditions correspond to normal extrusion conditions for this compound; full details of these are given in Ref. 11. The melt temperatures were 159, 170, and 185°C, for the LT, NT, and HT extrudates, respectively. The degree of fusion, of course, is a function of both the shear and the thermal history of the material. In this work only the thermal history was varied, as indicated by the defined temperatures.

Extruded specimens were chopped into flake form and then mechanically crushed into powders under liquid nitrogen. The powders were screened to provide particles in the range of 180–600 μm (30–80 mesh). Between 3–4 g of the screened powders was packed directly into 1-m-long stainless steel columns and used as stationary phases in the IGC experiments. Following well-established practices,[12] PVC stationary phases were probed with n-alkanes as the volatile phase. Reagent-grade n-alkanes from C_9 to C_{12} were used, as received.

IGC measurements were carried out with a Varian 3400 gas chromatograph, equipped with a FID detector. Helium was the carrier gas and methane the marker; carrier gas flow rates were controlled from 5 to 70 mL/min. Measurements of retention characteristics were made at 40 and 100°C, the former

below, the latter above the T_g of rigid PVC, which was determined to be near 80°C. Prior to measurements, columns were conditioned at 140°C for 24 h, considerably below the temperature for onset of apparent fusion. This was intended to drive off adventitious adsorbed materials, without significantly changing the melt processing history of the materials.

In the majority of data analyses, use was made of the specific retention volume,[12] V_g. Retention times required for calculating this parameter were obtained from at least three replicate determinations. Invariably symmetrical elution traces were obtained for the alkane vapors injected at very high dilution. V_g values are accurate to ±3%. The V_g data also were used to compute the dispersive contribution to the polymer surface free energy, (γ_s^d). The use of IGC data for this purpose has been fully described in recent publications.[13,14]

RESULTS AND DISCUSSION

It is well known that two parameters are implicated in the diffusion of small molecules through a polymeric structure. The molecule must first be adsorbed on the polymer surface and remain there sufficiently long to initiate penetration into the bulk. Then, sufficient accessible volume must be available to permit the diffusing species to propagate into and through the bulk. IGC data collected below the polymer T_g are widely held[12] to be determined solely by surface adsorption phenomena. Accordingly, the retention volume should be insensitive to variations in the contact time between probe molecule and polymer surface, as controlled by variations in the carrier gas flow rate. This expectation is met by present results, as shown in Figure 1 for the LT polymer at 40°C.
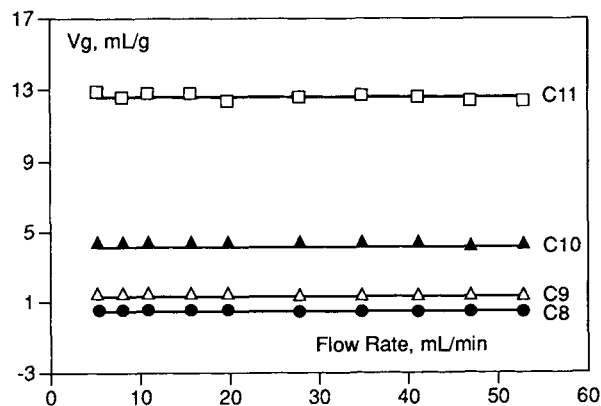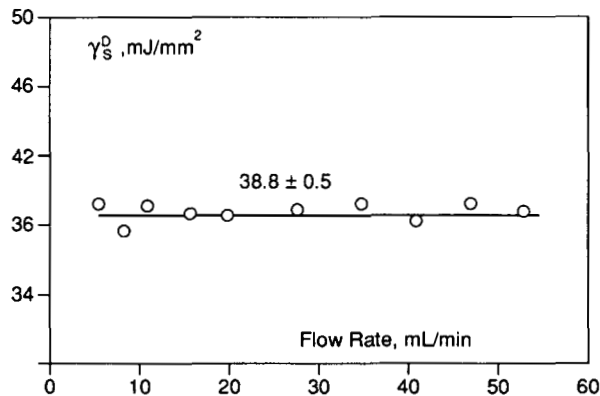

Figure 1 Specific retention volume of n-alkanes as function of carrier gas flow rate; PVC-LT at 40°C.

The V_g, of course, varies significantly among the alkanes, but in every case remains independent of flow rate. It is reasonable to assume that significant interparticle void spaces would exist within the bulk polymer, particularly in the LT samples. Thus, were diffusion to take place, then a systematic increase in V_g would be expected as the flow rate of carrier gas diminished.[15] Figure 1 indicates that no bulk diffusion is taking place. Calculation of (γ_s^d) reinforces the conclusion that no bulk diffusion is involved, since the surface energy parameter for LT at 40°C was found to remain constant, independent of flow rate. This is documented in Figure 2.
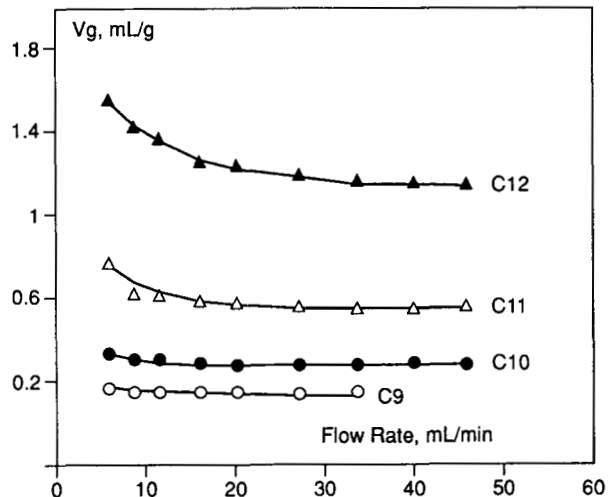
A very different pattern of results is obtained in IGC experiments at 100°C. These are presented in Figures 3, 4, and 5 for PVC processed under LT, NT, and HT conditions, respectively. The interpretation offered in Ref. 15 applies to these results: Above the polymer T_g, both adsorption and diffusion (absorption) into the polymer bulk can take place. The contribution of bulk diffusion to the overall V_g increases with diminishing flow rate. At high carrier gas flow rates, however, the residence time of an adsorbed molecule is insufficient to initiate the diffusion process, so that the V_g value attains a constant plateau, defined by the surface adsorption process alone. In other words, above T_g, we state that

$$(V_g)_o = (V_g)_s + (V_g)_b \tag{1}$$

where the subscripts o, s, and b designate overall, surface, and bulk values, respectively, of the retention volume. $(V_g)_s$ is given by the plateau values clearly discerned in Figures 3–5. An extrapolation of data to zero flow rate is wanted in order to best define the bulk contribution. This is done conve-
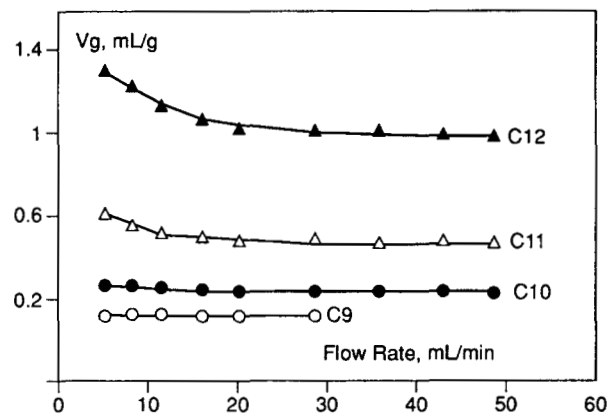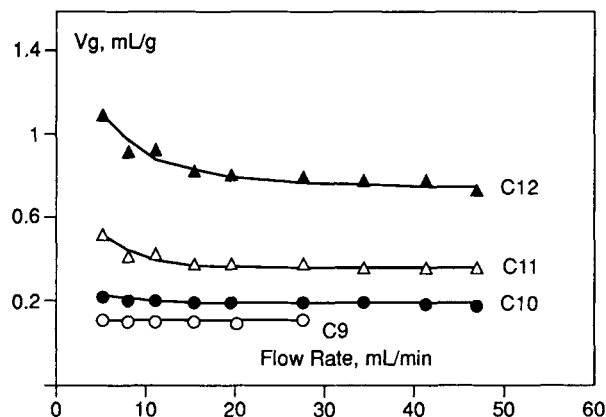

Figure 3 Specific retention volume of n-alkanes as function of carrier gas flow rate; PVC-LT at 100°C.

niently by plotting a logarithmic function of V_g vs. flow rate, as illustrated in Figure 6 for the NT sample. The overall $(V_g)_o$ so determined, the surface and bulk diffusion contributions to V_g are entered in Table II. The final entry in the table is the dispersion contribution to surface energy as calculated from the $(V_g)_s$ data.

Substantial differences are to be seen in the retention data for each of the PVC samples and each of the vapor probes. In all cases the progression for each of the V_g parameters is LT-PVC > NT-PVC > HT-PVC. Focusing on the bulk diffusion parameter, this increases by about 40–50% when comparing LT and HT values, but only by about 10% in the NT-HT comparison. The void volume within the PVC evidently decreases when the melt temperature is raised from 159 to 185°C, and the great

Figure 2 Dispersive component of surface energy of PVC-LT at 40°C, determined from IGC data at various carrier gas flow rates.

Figure 4 Specific retention volume of n-alkanes as function of carrier gas flow rate: PVC-NT at 100°C.
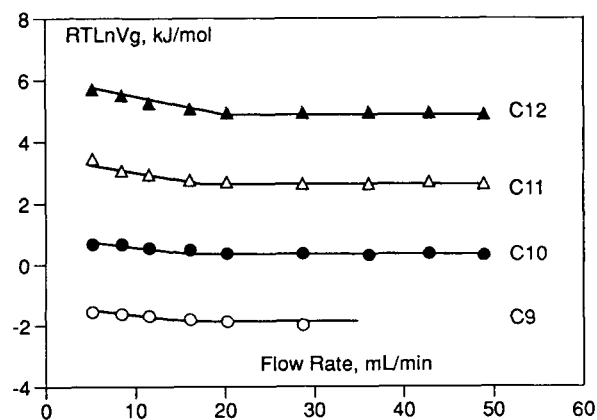
Figure 5 Specific retention volume of n-alkanes as function of carrier gas flow rate; PVC-HT at 100°C.

majority of that decrease takes place in the temperature interval 150–170°C. The inference is that under the NT processing conditions of this work the PVC specimens were incompletely fused. The tabled data will provide a quantitative assessment of the degree of fusion attained under LT and NT extrusion conditions, if it is assumed that the HT process results in "complete" fusion. Dynamic modulus data for these materials showed[11] that the HT sample was, in fact, incompletely fused. This assumption is used therefore as an illustration only. The degree of fusion achieved in the NT and LT samples may be calculated by ratioing the experimental $(V_g)_b$ data. Thus, using results for all of the alkane probes, under NT conditions the degree of fusion is 88 ± 5%. In comparison, LT extrusion produces compounds with a degree of fusion = 69 ± 2%. These estimates could be refined by the availability of data for compounds produced under combinations of more intensive shear and/or higher temperature than those corresponding to the HT extrusion mode. This would make it possible to realize the full potential of the IGC approach to the quantitative specification of states of fusion in PVC compounds.

The progression noted above for $(V_g)_b$ values also applies to the surface localized contributions, $(V_g)_s$. One possible reason for this might be a systematic change in the surface energy of PVC samples exposed to various melt temperatures. This is disspelled by the reported surface energy results, however, which are consistent with literature data[16] and show no significant differences among the three PVC extrudates. A more plausible explanation is an increase in the effective surface area of samples produced under NT and LT conditions. Incomplete fusion and increasing interparticle void volume would

also tend to create a more porous surface region, thus accounting for the observation.

One aspect of the data in Table II is at first surprising: We refer to the systematic and significant increase in $(V_g)_b$ with increasing size of the diffusing alkane molecule. This result underscores the difference between conventional and IGC measurements of diffusion characteristics and between diffusion and diffusivity. In conventional (e.g., desorption) experiments, the contact time between bulk and diffusing species is effectively infinite and equilibrium conditions are established.[17] Consequently diffusivity results are obtained which are inversely proportional to the size of the diffusing molecule, but independent of contact time between diffusant and barrier. In contrast, equilibrium diffusion conditions are not realized in the IGC measurement, when the contact time between barrier and diffusant is controlled by the carrier gas flow rate. Since it is the longer chain alkane which has the greater surface affinity for the polymer, the residence time on the polymer surface varies with the chain length of the adsorbing molecule. Thus, even though the diffusivity of longer alkanes is less than that of their shorter homologues, the probability of initiating diffusion into the bulk increases with chain length and offsets the diffusivity disadvantage. The case of methane illustrates the point. The smallest of alkanes has the highest diffusivity of the series, but its surface affinity for PVC is so slight that in our IGC measurements no adsorption takes place, and its retention time was found to be zero (hence the use here, and generally in many chromatographic experiments, of methane as a marker molecule). Clearly, no diffusion into the polymer can take place.

Figure 6 Linearization of specific retention volume vs. flow rate relationship for PVC-NT at 100°C. RT are gas constant and temperature (K), respectively.

Table II   Specific Retention Volumes at Zero Flow Rate of Carrier Gas

	PVC Sample (mL/g)								
	LT			NT			HT		
Probe	$(V_g)_o$	$(V_g)_s$	$(V_g)_b$	$(V_g)_o$	$(V_g)_s$	$(V_g)_b$	$(V_g)_o$	$(V_g)_s$	$(V_g)_b$
C_9	0.16	0.14	0.02_5	0.14	0.12	0.02_0	0.11	0.09_2	0.01_8
C_{10}	0.33	0.28	0.05_2	0.28	0.24	0.04_5	0.23	0.19	0.03_6
C_{11}	0.80	0.57	0.23	0.65	0.49	0.16_5	0.54	0.39	0.15_4
C_{12}	1.67	1.17	0.50	1.41	1.02	0.39	1.17	0.82	0.35_1
(γ_s^d) (mJ/m^2)		29.4			30.3			30.8	

A mathematical counterpart can be presented to the above rationalization. If equilibrium between vapor molecules and the bulk polymer in IGC work is reached exponentially, as is usually the case in kinetic processes,[18] then

$$(V_g)_o = (V_g)_s + (V_g)_b = (V_g)_s + (V_g)_b^* f(t) \quad (2)$$

and

$$f(t) = 1 - K \exp(-Kt) \quad (3)$$

Here $(V_g)_b^*$ is an initial value of the diffusion contribution to retention volume, $f(t)$ is a function of time which approaches unity when t is large, and k and K are temperature-dependent constants. In addition, following van Deemter and co-workers,[18] K is proportional to the diffusion coefficient of vapor in the stationary phase.

Combining Eqs. (2) and (3) leads to:

$$(V_g)_b = (V_g)_b^* [1 - k \exp(-Kt)] \quad (4)$$

In keeping with the discussion above, t of Eq. (4) is replaced by the retention time contributed by surface adsorption, $(t_r)_s$. A test of this expression for the LT-PVC sample is given in Figure 7. For convenience only the data for C_{11} and C_{12} probes are shown, but these clearly follow the predicted exponential relationship, as do those of the other alkane probes. Curve-fitting procedures carried out on data for LT, NT, and HT may be used to obtain values of the K parameter. These fall invariably in the progression:

$$K_{C9} > K_{C10} > K_{C11} > K_{C12}$$

consistent with expectations for the size dependence of the diffusivity.

CONCLUSIONS

1. The IGC method has been used to evaluate the degree of fusion in a rigid PVC formulation processed at three different melt temperatures. The evaluation is made possible by protocols which separate contributions to the overall retention volume made by surface adsorption and bulk penetration of vapor probes, when experiments are carried out above the polymer T_g.
2. The degree of fusion was shown to increase systematically as the melt temperature was raised from 159 to 170 and 185°C. The major portion of the increase occurred in the 159–170°C interval. Additional data will be required to show whether or not interparticle
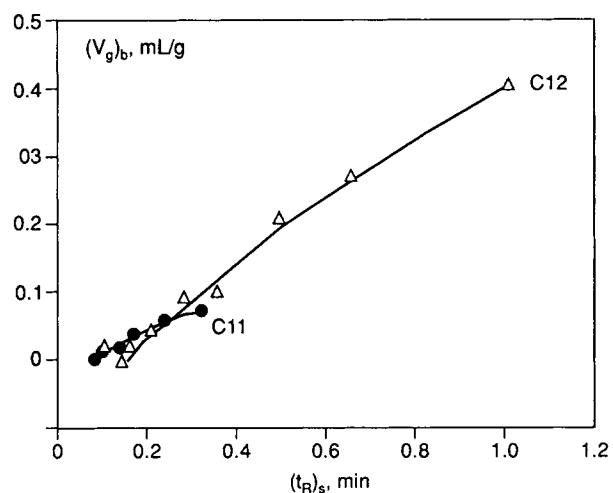
Figure 7   Specific retention volume due to bulk diffusion as function of the surface retention time of n-alkanes on PVC-LT at 100°C.

boundaries were fully eliminated by extrusion at the highest temperature.

3. It was shown that, unexpectedly, diffusion of n-alkanes into the bulk PVC increased with increasing chain length of the diffusants. This was attributed to the adsorption behavior of alkanes at the PVC surface. Residence time in the adsorbed state varies directly with chain length, thus increasing the ability of longer chains to initiate penetration into the bulk polymer.

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