

Effect of glass transition temperature on volatile emissions from vinyl flooring

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ABSTRACT

The material-phase concentration of volatile organic compounds (VOCs) is a key parameter influencing the emission characteristics of many indoor materials. Samples of vinyl flooring (VF) were milled to a powder under liquid nitrogen to simultaneously homogenize the material and reduce the diffusion path length without loss of VOCs. VOCs were extracted from the VF particles at room temperature (23°C) by fluidized bed desorption (FBD) and over a range of temperatures (30–150°C) by direct thermal desorption (DTD). The glass transition temperature (T_g) of the VF was determined to be 54°C. The mass of material extracted below T_g was significantly lower than mass extracted above T_g . The difference is likely due to the increase in free volume above the glass transition temperature and suggests that some fraction of the VOCs initially present in VF will not be emitted, or will only be emitted extremely slowly.

INDEX TERMS

Diffusion; Direct thermal desorption; Fluidized bed desorption; Polymer, VOC

INTRODUCTION

Vinyl flooring (VF) is manufactured in a variety of styles and compositions and is widely installed in residential and commercial buildings. In the United States alone, 214 million kilograms of PVC were used in the production of VF during 1998 (Resins Report, 1999). VF is known to emit a number of volatile organic compounds (VOCs). Characterizing VF as a source of indoor VOCs requires assessing both the rate at which VOCs are emitted and the total amount of VOCs that can potentially be emitted. Traditional methods for measuring concentrations of VOCs in solid materials have used solvents or heat to extract target compounds. However, free-volume theory reveals that the structure of a polymer can be affected by temperature and the presence of chemical solvents. Free-volume is the sum of the void spaces that exist between the imperfectly arranged polymer chains (Sperling, 1992). The amount of void space depends on the conformational arrangement of the polymer chains. At lower temperatures free volume is largely independent of temperature. However, at temperatures above the glass transition temperature (T_g), polymer molecules possess sufficient energy so that coordinated chain movement becomes possible, resulting in a relatively large net increase in free-volume. Indeed, T_g can be characterized as the temperature at which an inflection point in the free-volume–temperature curve occurs. Polymers at temperatures below T_g are referred to as ‘glassy’ and at temperatures above T_g as ‘rubbery’. Due to the additional free-volume, the rate of diffusion through the polymer is high when the material is above T_g .

In this study, a sample is obtained from a VF sheet by punching small discs from a large area of the material. The sample is pulverized into small particles in a ball mill under a liquid nitrogen bath. Extraction of VOCs from the milled particles is accomplished at room

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temperature by fluidized bed desorption (FBD) and over a wide range of temperatures by direct thermal desorption (DTD).

METHODS

The VF material used was a monolayer sheet vinyl manufactured for the medical facilities market. The VF was pulverized using a cryogenic ball mill. VF was randomly sampled using a hollow arch punch to cut approximately 200 discs of 1-cm diameter each. The discs and two 20-mm diameter stainless steel balls were transferred to a stainless steel vial in the milling chamber of the ball mill. The milling chamber was flooded with liquid nitrogen for approximately five minutes before milling began. After cryogenic milling (CM), the powdered VF material was transferred to 4.5-ml, zero-headspace glass vials and stored at -15°C . VOCs in VF particles were extracted at room temperature using FBD (Cox *et al.*, 2001). A known mass (~ 1 g) of VF particles was transferred to a FBD vessel (2.6 l) constructed of borosilicate glass. Clean air regulated by a mass-flow controller (MFC) at ~ 6 l min^{-1} was passed through the vessel to fluidize the VF particles. VOCs were collected by pumping a fraction (~ 15 ml min^{-1}) of the effluent fluidization air through a sorbent tube. Four samples were successively collected over each 7-h FBD test during the time periods 0–60 (blank, no VF particles in the FBD apparatus), 60–120, 120–240 and 240–420 min.

VOCs were also extracted from VF particles by DTD (Cox *et al.*, 2001). A mass of milled particles was weighed into a small aluminium foil boat. The boat was inserted into a 4-mm ID 20-cm long borosilicate glass tube. The glass tube was placed in a 150-W sleeve heater fitted with a thermocouple between the sleeve and the resistance winding. The inlet flow of humidified N_2 ($\sim 10\%$ RH) to the tube was regulated by a MFC at 100 $\text{cm}^3 \text{min}^{-1}$. A fraction of the outlet gas stream ($1/25$) was drawn through a sorbent tube using a MFC and vacuum pump. At the start of desorption, the heater temperature was quickly ramped from ambient to 30°C and held for 10 min. Next, the temperature was ramped over 20 min to $150 \pm 5^{\circ}\text{C}$ and then held constant. Gas samples were collected successively over 0–60, 60–120 and 120–180 min. after initiating a test. A more detailed DTD temperature study was also conducted. In this case, batches of milled particles were heated in the same apparatus from ambient temperature to a range of final temperatures (30 – 150°C).

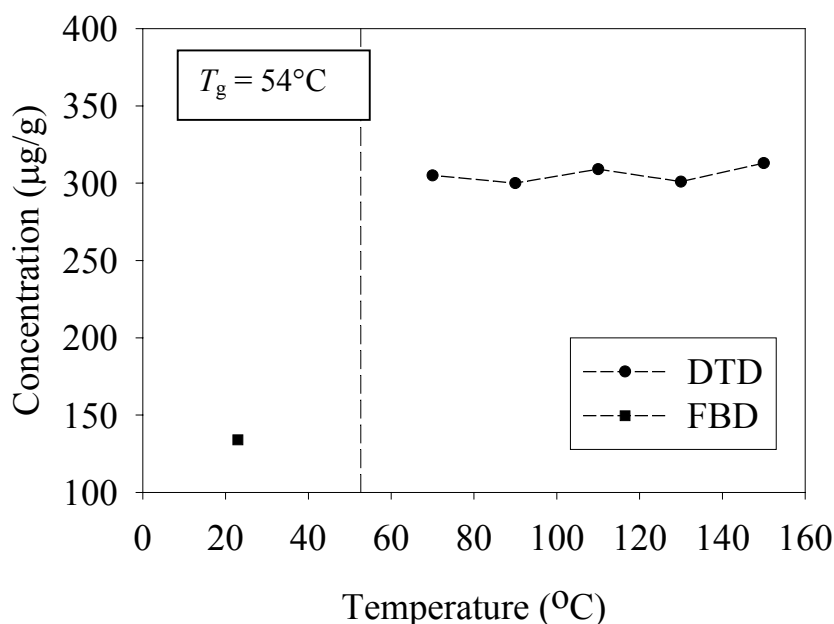
RESULTS AND DISCUSSION

The material-phase concentrations of selected VOCs obtained by FBD and DTD in a first VF sample are presented in Table 1. Results obtained by FBD at room temperature were 30–70% lower than those obtained by DTD, which were measured at 150°C . The results for phenol are shown as a function of temperature in Figure 1. Also shown on this plot is the glass transition temperature of the VF sample. This was measured and found to be about 54°C .

These results show that when the desorption temperature is raised above T_g , substantially more of the VOCs are extracted. According to Vieth (1991), if a polymer is cooled from the rubbery state to the glassy state, a distribution of microvoids is frozen into the structure. Because free segmental chain movement is restricted in the glassy state, the microvoids in the glassy polymer immobilize a portion of diffusant molecules by entrapment. In contrast, if the temperature of the VF is raised above T_g , the polymer molecules are able to move more freely, resulting in a relatively large increase in free-volume. This idea is supported by the data presented in Figure 1 because it suggests that a considerable fraction of the phenol in the VF is essentially trapped in microvoids when the temperature is below T_g . Once the temperature is raised above T_g , the trapped fraction is released.

Table 1 Material-phase concentration of selected VOCs in first VF sample

Compound	FBD ($\mu\text{g/g}$)	DTD ($\mu\text{g/g}$)
Phenol	134 ± 29	321 ± 16
<i>n</i> -Tridecane	22.7 ± 2.9	33.4 ± 0.5
<i>n</i> -Tetradecane	29.5 ± 2.5	43.5 ± 0.6
<i>n</i> -Pentadecane	28.5 ± 0.6	47.7 ± 0.6
<i>n</i> -Hexadecane	5.1 ± 0.6	17.6 ± 0.1

**Figure 1** Material-phase phenol concentration as a function of desorption temperature in first VF sample and relationship to glass transition temperature.

To confirm these results, a preliminary series of desorption experiments was carried out using DTD over a temperature range from 30 to 70°C using a completely new sample of VF. The results are shown in Table 2. Recall that T_g for VF is about 54°C. Below T_g , the extracted quantity is essentially constant. Above T_g , there is a marked increase in extracted quantity, which tends to confirm the previous observations. These preliminary experiments are being repeated and extended to provide further evidence for this interesting phenomenon.

Table 2 Material-phase concentration (in $\mu\text{g/g}$) of selected VOCs in second VF sample by DTD

Compound	$T = 30^\circ\text{C}$	$T = 40^\circ\text{C}$	$T = 60^\circ\text{C}$	$T = 70^\circ\text{C}$
<i>n</i> -Tridecane	20.8	22.2	59.0	70.9
<i>n</i> -Tetradecane	22.2	17.2	56.1	79.3

CONCLUSIONS

Knowledge of the initial concentrations of VOCs in a solid material such as VF is crucial for assessing the emission characteristics of the material and its potential to contaminate indoor air. Solid-phase concentration measurement methods such as thermal headspace analysis and

solvent extraction may affect the physical structure and consequently the emission characteristics of polymeric materials. The FBD technique does not employ solvents or high temperature for VOC extraction and improves the representative sampling of larger pieces of materials. With this technique, VOC content can be determined under conditions similar to those to which the material is exposed when installed in an indoor environment. DTD also appears able to measure this quantity, provided the extraction procedure is carried out below T_g . The concentration determined in this way can be used as a parameter in mechanistic models to estimate VOC emission rates (Cox *et al.*, 2002).

The results of FBD and DTD concentration measurement are consistent with the free-volume concept for polymers. Below the glass transition temperature, one fraction of the diffusant population is considered mobile while the other is considered immobilized, or only partially mobile. While somewhat speculative, it appears that either FBD or DTD can provide a measure of the readily emittable fraction of the VOC as long as the desorption temperature is held below T_g . DTD carried out above T_g quantifies the total amount present in the VF.

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REFERENCES

- Cox, S.S., Hodgson, A.T. and Little, J.C. (2001). Measuring concentrations of volatile organic compounds in vinyl flooring. *Journal of Air & Waste Management Association* **51**, 1195–1201.
- Cox, S.S., Little, J.C. and Hodgson, A.T. (2002). Predicting the emission rate of volatile organic compounds from vinyl flooring. *Environmental Science & Technology* **36** 709–714.
- Resins Report (1999). *Modern Plastics* **76**, 43–80.
- Sperling, L. (1992). *Introduction to Physical Polymer Science*, 2nd edn. New York: John Wiley & Sons.
- Vieth, W. (1991). *Diffusion in and Through Polymers*. Munich: Hanser Publishers.