EMISSION OF ISOCYANATES FROM PUR-ADHESIVES. TIME COURSE OF EMISSION FROM CURING PUR-ADHESIVE

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ABSTRACT

The time course of isocyanate emission from curing PUR-adhesives was studied in an emission test chamber. The adhesives under investigation were commercial products for fixing of textile floor coverings and based on methylene bisphenyl diisocyanate (MDI). Influence of the curing mechanism was studied by comparing the emission curves of one-component adhesive (OCA) and two-component adhesive (TCA). For TCA the decrease in isocyanate emission was found to follow a two-step process during curing. In the first step the emission is dominated by surface evaporation and the decay of emission is mainly caused by the decrease in monomer content due to reaction. In the second step the release is limited by internal diffusion. The influence of monomer reactivity on the emission profile could be demonstrated for 2,4´- and 4,4´-MDI. The less reactive 2,4´-MDI caused prolonged emission.

INDEX TERMS

VOCs and SVOCs, Indoor air chemistry, Measurement methods, Air and pollutant transport modeling and measurement, Monomers

INTRODUCTION

Polyurethane adhesives are widely used because their chemical and rheometric properties can be adapted to various materials. The high reactivity of diisocyanates leads to very durable bonding, but also gives rise to health risks for persons under exposure (Wolff and Stirn, 2000). Therefore there is a demand for information on isocyanate emission from fresh PUR adhesive systems. Such adhesives systems are based on "polymeric MDI" (PMDI). In the synthesis of PMDI not only the symmetric 4,4´-MDI is obtained but also the asymmetric 2,4´-MDI in smaller amounts and, to an even lesser extent, 2,2´-MDI (Ulrich, 1999). Additionally different amounts of MDI homologues with three and more benzyl rings depending on the reaction conditions will be obtained.

Previous work has shown that the emission of monomers from fresh PUR-adhesives can be described in a similar way as for isocyanate resins (Wirts and Salthammer, 2002). The emission process was found to be limited by gas-phase diffusion, i.e. fresh polyurethane (PUR) adhesives are best described as "wet sources". In contrast to curing processes of wet paints, which are dominated by physical "drying" caused by solvent evaporation (Clausen, 1993; Sparks et al., 1999; Zeng et al., 1999), PUR adhesives harden by a reaction which leads to a depletion of the emitting monomer-substance. Furthermore, the reaction leads to an alteration of the matrix which may influence the diffusion of monomers through the bulk. For separation of these two effects we conducted two experiments. The depletion of monomer in the adhe-

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sive was investigated by analysis of the monomer in the adhesive bulk. For investigation of matrix effects the emission behaviour of inert tracer compounds added to the adhesives were monitored.

METHODS

Two-component adhesive (TCA): Component A (70 %) is based on a mixture of polyols on the basis of propylene glycol with a functionality of two and three. Component B (29 %) is polymeric MDI (4,4′-MDI, isomers and homologues) with an 4,4′-MDI content of 18.7 % (2,4′-MDI < 0.8 %). The adhesive is catalysed by trialkyl amines (0.7 %). The working life (time in which the adhesive can be applied) is approximately 30 min. *One-component adhesive (OCA):* The adhesive is based on an MDI-prepolymer containing 4,4′-MDI (14.9 %) and 2,4′-MDI (15.4 %) and is catalysed by trialkyl amine (0.2 %).

The isocyanate emission of PUR adhesives was evaluated by measuring the area-specific emission rate SER_a in a laboratory emission chamber with a volume of 2.2 l (Wirts et al., 2001). The adhesives were spread in the chamber across an area of 48 m². Diisocyanates emitted were analysed as their 1-(2-pyridyl)piperazine (2PP) derivatives by HPLC with UV- and fluorescence detection (Schulz and Salthammer, 1998). Naphthalene and butyl benzene were used as tracer compounds and sampled on activated charcoal and analysed by GC/MS after CS_2-elution. The time course of MDI content in the two-component adhesive was evaluated by adding approx. 10 mg of the curing adhesive to a solution of 2PP in DMSO at different times followed by HPLC analysis.

RESULTS AND DISCUSSION

Emission curves for the release of ΣMDI (sum of 4,4′-, 2,4′- and 2,2′-isomers) over time from curing TCA and OCA are shown in Figure 1. The decrease in isocyanate emission from both adhesives is mainly caused by the decreasing isocyanate content due to reaction. Loss of diisocyanates by evaporation is small because of the low vapour pressure of these species $(p(4,4′\text{-MDI}) = 8*10^{-6}$ hPa at 20°C). To confirm this the emission rates of 4,4′-MDI and 2,4′-MDI from a TCA were monitored in parallel (data not shown).

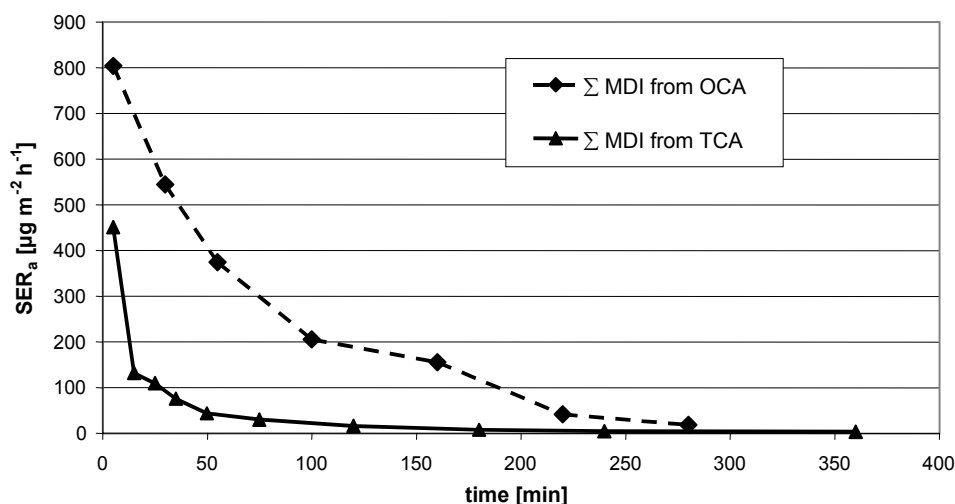**Figure 1.** ΣMDI emission over time from adhesives OCA and TCA at 40°C.

As can be seen from a comparison of TCA and OCA the curing mechanism has a strong influence on emission behaviour. The OCA hardens by the reaction with water vapour. Curing is therefore limited by the diffusion of the water into the bulk material and characterised by film forming. In contrast the reactants in TCA are homogeneously mixed from the beginning

of the reaction leading to a fast decrease of emission. Curing of TCA is an isotropic process, whereas OCA curing is anisotropic. Therefore the thickness of the adhesive applied influences the curing of OCA, but not of TCA. It can be concluded that the curing mechanism has to be taken into account when interpreting emission data.

For detailed investigation of reaction progress of TCA, bulk analysis was applied by adding a sample of the reacting adhesive at certain times to a 2PP solution in DMSO, thus stopping the reaction. The results of the bulk analysis are shown in Figure 2 as fluorescence detection signals normalised to the weigh-in quantity.
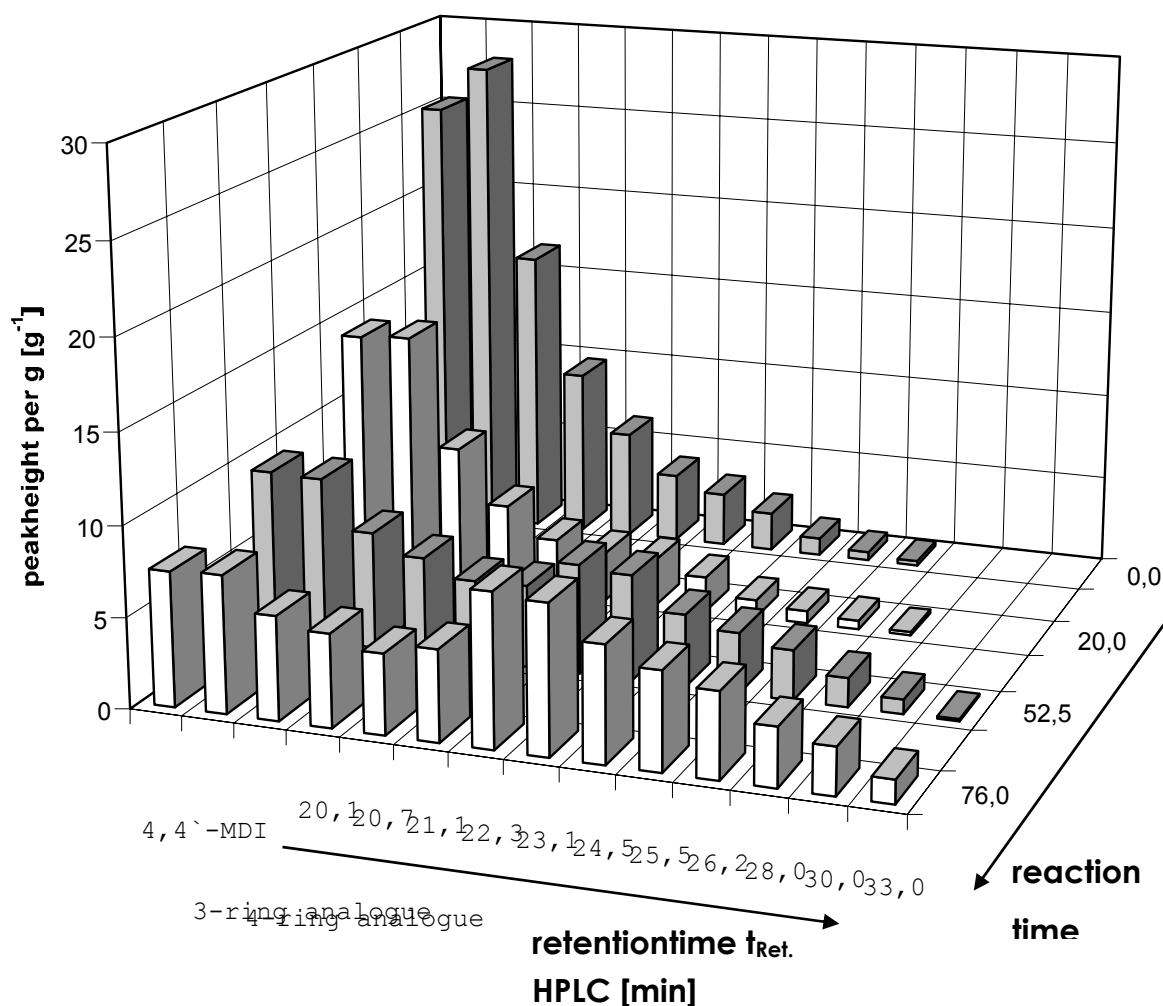

Figure 2. Results from HPLC bulk analysis of curing TCA.

As can be seen from the analysis of the wet adhesive (reaction time $t_R = 0$ min), the isocyanate raw material is an MDI with homologue proportion, whereby the 3-ring and the 4-ring MDI can be clearly identified using a standard. As the reaction progresses the concentrations of the low homologues decrease slowly (peaks with $t_{Ret.} \leq 21.1$ min), while in higher retention time ranges a slow formation of polymolecular prepolymers can be seen. 2,4′-MDI was present in this system only with peak values < 1 g^{-1}. The duration of the experiment is limited by the decreasing solubility of this cross-linking adhesive system in DMSO. For a closer look at the time course of evaporation we have plotted in Figure 3 the content of 4,4′-MDI in the bulk of TCA (first row in Figure 2) together with the emission of 4,4′-MDI (see Figure 1) over time at 40°C.
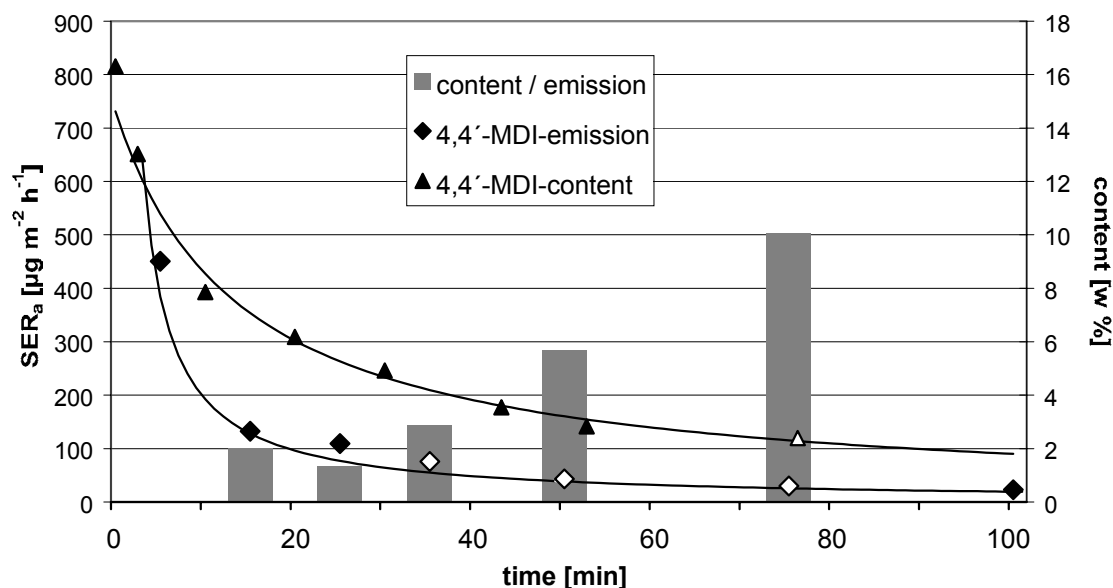
Figure 3. Time course of MDI emission and content of TCA, 40 °C; highest bar (ratio) was normalized to 10.

Plotted lines are fitted with a double exponential equation. The reaction mechanism is sophisticated due to the involvement of MDI-homologues with functionality > 2 and differences in the reactivity of isocyanate groups (Grunwald, 1999).

The emission and content of 4,4´-MDI show a parallel course in the early stage represented by an almost constant ratio of content/emission (see bars in Figure 3). This is consistent with the results of isocyanate emission from non-reacting resins, where emission was found to be proportional to the monomer content (Wirts and Salthammer, 2002). After approx. 30 min the ratio rises, i.e. the emission decreases faster than expected from the content. This is caused by a change of the evaporation from surface to bulk limited diffusion. The change occurs much earlier than reported by Sparks et al. (1999) for physically drying paints, which can be rationalised by the fast alteration of the matrix in this polymer reaction. It has also to be considered that the resulting polymer is a duromer network with lower diffusion for organic substances in contrast to the polymer chains resulting from physically drying paints.

To confirm this hypothesis, the change in evaporation was studied by adding naphthalene to the adhesive TCA (0.071 %) and the naphthalene emission was measured as a function of time. Naphthalene does not react with isocyanates. To compare the emission from a reacting and an inert matrix, experiments with the polyol (containing 0.1 % naphthalene) were conducted in parallel. Naphthalene emissions are shown in Figure 4 in normalized form referring to the highest emission rate together with the course of viscosity. The increase of viscosity is an indicator for the progress of the reaction.

The results show a constant naphthalene emission from TCA which starts to drop after 25 to 35 min, whereas the emission from the inert polyol is hardly affected. The naphthalene emission from polyol has been lowered to 77 % of the initial rate after 300 min and the naphthalene content is lowered to 74 %, as can be calculated from $\int SER_a\, dt$. The naphthalene emission therefore seems to be almost proportional to the content. In contrast, emission from TCA is lowered to 1 % after 300 min, but the content is still 97 % of the initial value. These findings elucidate the influence of matrix alteration on the emission from adhesives as stated

above for the MDI emission from TCA. The change from evaporation to internal diffusion seems to occur earlier for naphthalene than for MDI. As naphthalene is a more volatile compound the maximum level of internal diffusion should be reached earlier than for MDI, when assuming similar internal diffusion coefficients for both substances. This was verified in an analogous experiment by using the more volatile butyl benzene instead of naphthalene (see Table 1). The proportionality of emission and content was also found here.
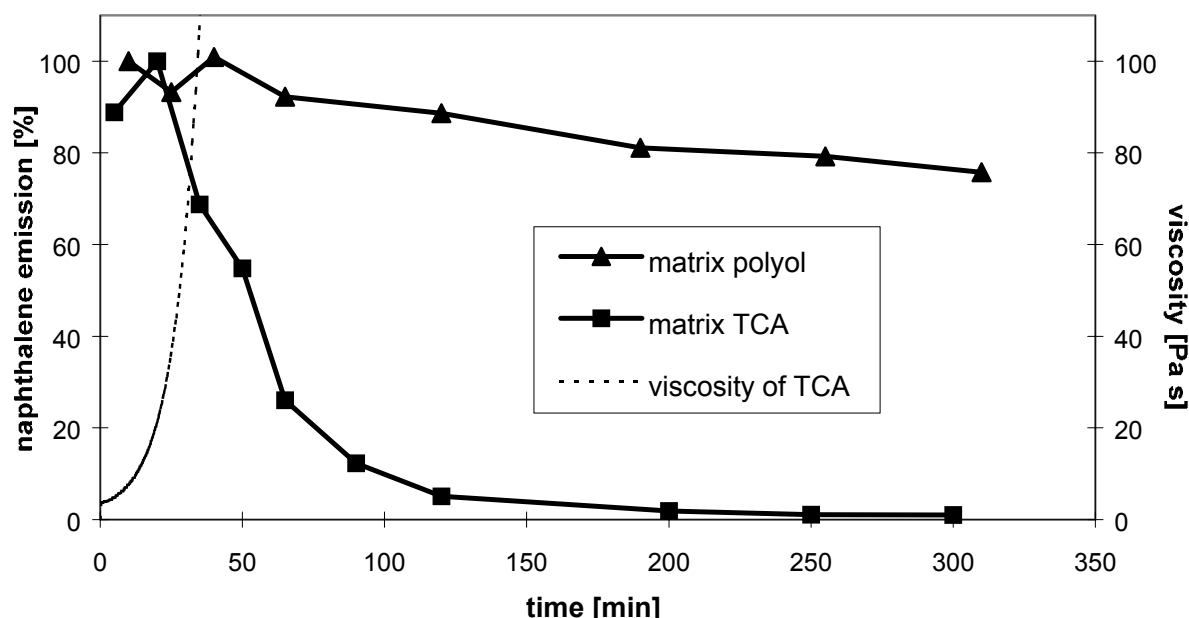

Figure 4. Emission of the inert compound naphthalene from reacting (TCA) and non-reacting matrix (polyol) and viscosity of TCA.

When investigating monomer emissions from reactive adhesives the main points to consider are the matrix alteration and the decrease of the substance under investigation due to reaction. Simple source models such as the single exponential decay is therefore not expected to be adequate to describe the emission profile. The findings are summarised in Table 1 together with the results from the rheometric analysis.

Table 1. Change of evaporation for MDI, naphthalene and butyl benzene and viscosities.

compound	p^* [hPa], 25°C	change	viscosity	non-reactive polyol matrix after 300 min % of initial	
				emission	content
4,4´-MDI	8×10^{-6}	30 – 40 min	60 to 190 Pa s	--	--
naphthalene	0.106	25 – 35 min	40 to 110 Pa s	77	74
butyl benzene	1.40	≤ 20 min	≤ 22 Pa s	24	26

CONCLUSIONS

The emission of isocyanates from fresh polyurethane adhesives can be described similarly to the emission of pure resins. Both are limited by gas-phase diffusion (Wirts and Salthammer, 2002). During the curing reaction of adhesives the monomer emission decreases mainly due to the decreasing amount of the monomers in the bulk caused by polymer reaction. The course of emission in the early stage is therefore controlled by the reactivity of the isocyanate monomer. In this early stage the emission is controlled by surface evaporation, whereas in the second period internal diffusion is the limiting step. Another important factor for the emission profile

is the curing mechanism as shown by comparing the emission profiles of a one- and a two-component adhesive.

The findings provide a closer look at the emission profile of reactive adhesive systems. The fast decrease in isocyanate emission confirms that exposure levels in the indoor environment are believed to be low. Therefore Wolff and Stirn (2000) conclude that guidelines for long-term exposition in dwellings do not have to be introduced.

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