Migresives - Experimental determination of diffusion and partition coefficients in VAE adhesives and paper & board

MIGRESIVES

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Introduction

Vinylacetate-ethylene copolymer (VAE) type adhesives are an important class for glueing paper and board materials. They are used as aqueous dispersions e.g. for seams of paper pouches or folding boxes but also for the combination of paper or board with plastics e.g. when a window is inserted in a package. These VAE glues had been one of the adhesive types under investigation in the MIGRESIVES project (COLL-CT-2006-030309, 2007-2010) which intended to develop a pragmatic, science based test concept to ensure the safety-in-use of adhesives used in food contact materials. Three of five VAE formulations in the project had been investigated at Fraunhofer IVV with regard to their migration properties. From these studies the applicability of the migration model for plastic layers should be checked on adhesives and paper and board substrates. Furthermore the diffusion coefficients in adhesive and substrate layers as well as partition coefficients between these layers should be derived as basis for mathematical modelling of the migration processes.

Test systems and analytical tests

The VAE adhesives VAE 4 and VAE 5 were applied on paper. VAE 1 was applied on cardboard. VAE 1 and VAE 4 contained triacetin, VAE 5 benzoate type plasticisers. The plasticisers were the target substances for the migration studies.
To function as test systems the substrates (paper or board) were full area coated with the adhesive on one side. Some experiments had been performed with three layer systems cardboard/adhesive/cardboard. As acceptor media for the migration ('simulants') blank layers of the substrates, LDPE layers and the adsorbent MPPO (Simulant E for dry foodstuffs) had been used. The experiments were carried out as kinetic experiments with up to 6 measured time points at 23°C, 40°C, 60°C and 70°C (Figure 1) as well as concentration profile experiments ('Moisan' type) with a stack of substrate or LDPE film layers as acceptor media at 40°C and 70°C at equilibrium time (Figure 2). The concentrations of the target compounds were determined in all acceptor layers and in the test systems by GC-FID (30 m DB-1) after extraction with dichloromethane or 95 % ethanol (MPPO). The two benzoate type plasticisers were not separated chromatographically and determined as sum, therefore.

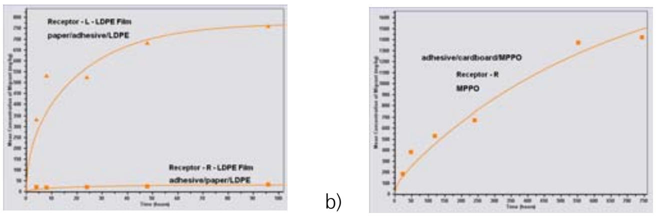

Figure 1: Examples of kinetic migration from a) VAE 5 adhesive/paper system into LDPE receptor films on both sides of the system at 60 C and b) VAE 1 adhesive/cardboard onto MPPO (simulant E) at 40 C

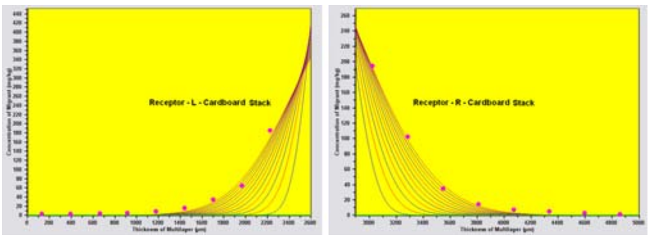

Figure 2: Example of static migration (Moisan) from a VAE 1 adhesive/cardboard system into stacks of receptor cardboards on both sides of the system at equilibrium temperature

Calculation of diffusion and partition coefficients

From the concentrations in the layers and the initial concentration before start of the equilibrium experiments the partition coefficient was obtained. At kinetic tests the concentration in a receptor layer was determined at several timepoints. To the experimental values the theoretical migration curve was fitted by adapting the parameters diffusion and partition coefficients.

These modelling calculations were carried out using the software Migratest Exp. The experimental data could be described by the migration modell. Paper and cardboard, which do not fulfill the prerequisite of homogeneity, could be tackled as quasi-homogeneous materials. The determined diffusion coefficients can be considered as apparent diffusion coefficients which are in fact the result of a weighted contribution of all diffusion coefficients from the non-homogeneous components of paper and board. The obtained diffusion and partition coefficients were evaluated for their temperature dependency. All results were included in the determination of AP and τ values for the diffusion coefficient estimation and for the reference partition coefficient approach.

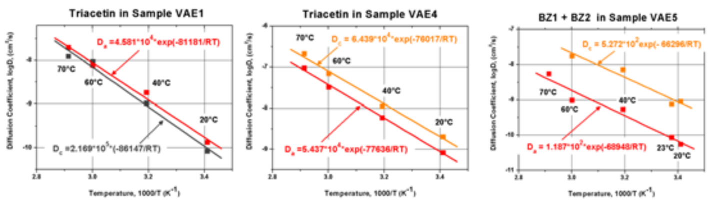

Figure 3: Diffusion coefficients D and their temperature dependency of triacetin and sum of two benzoate type plastisisers in VAE adhesives and substrates (red: adhesive layer, grey: cardboard, orange: paper)

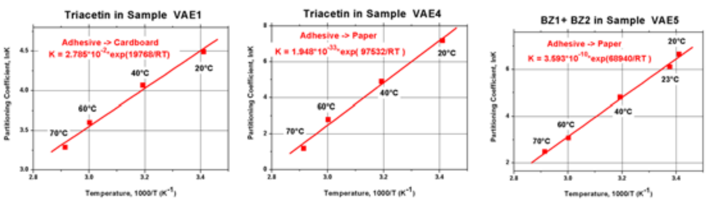

Figure 4: Partition coefficients K and their temperature dependency of triacetin and sum of two benzoate type plasticisers between VAE adhesives and their substrates cardboard or paper, respectively.

Conclusions

Migration in VAE type adhesive layers as well as in paper and board substrates can be described by the diffusion model which was developed for migration calculation in plastic layers. For paper and board the simplifying assumption of a quasi-homogeneous material and the use of apparent diffusion and partition coefficients was observed to be applicable. From the Arrhenius plots (Figure 3 and 4) the diffusion or partition coefficients at any temperature between 20 °C and 70 °C can be obtained. The partition coefficient of triacetin between adhesive and cardboard showed a only negligibly small temperature dependency whereas that of both plasticisers, triacetin and benzoate type clearly decreased at increasing temperature at partitioning between adhesive and paper substrates. All diffusion and partition coefficients were included in the determination of A_P and τ values for the diffusion coefficient estimation and for the reference partition coefficient approach.

Acknowledgements

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