Migresives - Parameters for mathematical modelling of substances from adhesives - A_P and τ values for calculation of diffusion coefficients in adhesives

Angela Störmer[1], Peter Mercea[2]

[1] Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany, email: angela.stoermer@ivv.fraunhofer.de, phone: ++49 8161 491 720

[2] Fabes Forschungs-GmbH, Schragenhofstraße 35, 80992 München, Germany

Introduction

The EU project MIGRESIVES (COLL-CT-2006-030309, 2007-2010) had the intention to develop a pragmatic, science based test concept to ensure the safety-in-use of adhesives used in food contact materials. Adhesives formulations are often very complex and contain numerous single components. In order to reduce or optimise the analytical expenses for migration testing, a main objective of the project was to establish the parameters for mathematical modelling of adhesive substances in multilayer materials. Partition and diffusion coefficients are the main parameters needed for the prediction of migration via mathematical modelling. From a set of experimentally obtained diffusion coefficients, a prediction was established to estimate the diffusion coefficients of additional substances in rubber, vinylic and acrylic type adhesives as well as in plastics, paper and board as substrates according to the estimate of diffusion coefficients for plastic materials via A_P and τ values.

Material and methods

For the study 23 representative test systems (substrate/adhesive/substrate) had been defined and selected by the consortium as typical for adhesives formulations, materials and structures used for food contact materials. Using these test systems systematic migration studies were performed as kinetic and concentration profile experiments using additives and also non-intentionally-added substances as target analytes.

The data from migration kinetic and concentration profile experiments were evaluated by mathematical modelling using Migratest Exp software by fitting the modelled curve to the experimental data. The equation for estimation of diffusion coefficients as proposed in the EU guideline on migration modelling (EU Report EUR 24514 EN 2010) correlates the diffusion coefficient with the molecular weight of the migrant, the temperature and the specific diffusion properties of a polymer expressed as "diffusion conductance" parameter A_P' and the activation energy parameter τ (tau) which describes the temperature dependency of the A_P value. All experimentally derived diffusion coefficients were then expressed as temperature independent A_P' and τ values (Equation 1 and 2). Such the diffusion coefficients were normalized on molecular weight of the migrant and the temperature for better comparison.

Table 1: Adhesive test systems for comprehensive studies within WP 2

Test system	Raw material polymer	Description of system	Substrate 1	Substrate 2	End application
Natural Rubber 1	Natural rubber/solvent based/ non-reactive with PUR primer	pressure senstive coating	plastic film	paper	psa tape for closings of folding boxes
Natural Rubber 2	Natural rubber/water-based/ non-reactive	cold seal, system without any fillers	BoPP film	BoPP film	tubular bag
Synthetic Rubber 1	Synth. Rubber/100 % system/ non-reactive	SEBS or SIS polymers, plasticised with mineral oil	paper	plastic film	bag with plastic window
Synthetic Rubber 2	Synth. Rubber/water-based/ non-reactive	SBR emulsion, wet and dry applications	metalised film	cardboard	trays
Acryl 1	Acrylic/ water based/ non-reactive	wet lamination	paper	opp film	bread bags with windows
Acryl 2	Acrylic/ water based/ non-reactive	film print lamination	paper	opp film	folding boxes and tray forfood
Acryl 3	Acrylic/ water based/ non-reactive	pure acrylate	label material:	e.g. cling film	psa paper labels
Acryl 4	Acrylic/water-based/ non-reactive	pressure sensitive coating	plastic film	paper	psa tape forfolding boxes
EVA 1	EVA/100 % system	injection hot melt	cardboard	(Laminated Opp) cardboard	folding box
VAE 1	VAE/water-based/ non-reactive	VAE plastisized with Triacetin:	cardboard	cardboard	folding box
VAE 2	VAE/water-based/ non-reactive	VAE different plasiticizer than TA	cardboard	plastic window	folding box
VAE 3	VAE/water-based/ non-reactive	VAE , plasticiser, antifoam agent, biocide, water	cardboard	cardboard	folding box
VAE 4	VAE/water-based/ non-reactive	VAE plastisized with Triacetin	paper	paper, coated paper	paper bags: side seam
VAE 5	VAE/water-based/ non-reactive	VAE plastisized with Benzoflex	paper	paper, coated paper	paper bags: side seam
PO 1	polyolefines/ 100 % system/non-reactive hot melt	hot melt system	paper	OPP film or polyolefin film	general use
PVAC 1	PVAc/water-based/ non-reactive	PVAc plasticized	cardboard	cardboard	folding boxes side seam

Equation 1: $D_P = D_0 \exp\left(A_P - 0.135 M_W^{2/3} + 0.003 M_w - \frac{10454}{T} \right)$

With: D_P diffusion coefficient [cm² s^{-1}] in the polymer layer P, D_0 = 10^4 cm² s^{-1}, MW molecular weight of the migrating substance [g mol^{-1}], T temperature [K].

Equation 2: $A_P = A_p' - \frac{\tau}{T}$ Equation 3: $E_A = (10454 + \tau) \cdot R$

With: A_P polymer specific "diffusion conductance" parameter, A_P' temperature independent diffusion conductance, τ activation energy parameter, T temperature [K]. Correlation of activation energy E_A [J mol^{-1}] and τ: R gas constant (8.314 J mol^{-1}K^{-1}).

In the same manner as done for the plastic materials (Begley, Castle et al. 2005) the "upper-bound" diffusion parameters AP'* and τ* were calculated (see Table 2 and 3) by using the 95 % confidence upper limit of the student t distribution of the experimentally derived values. In case of AP the higher value, in case of τ* the lower value represents the more conservative estimate. The upperbound values are marked with an asterix. From the τ* values the activation energy was calculated .

Results and Conclusions

Table 2: "Upper bound" parameters for the estimation of diffusion coefficients in adhesives

Adhesive-Group	A_P' value	SD (A_P' value)	upper-bound A_P'* value	τ	SD (τ)	upper-bound τ* value	n	student t (0,05, n-1, single sided)	Activation energy [kJ/mol]
Natural Rubber	10	0,1	10,3	-313	13	-351	3	2,920	
Synthetic Rubber	10,7	0,3	11,2	-376	23	-416	17	1,746	
Natural and Synthetic Rubber	10,6	0,4	**11,3**	-366	32	**-421**	20	1,729	**83**
EVA	6,3	0,2	6,6	-1154	48	-1236	27	1,706	
VAE	4,7	0,8	6,1	-1090	48	-1172	26	1,708	
PVAC	4	0,1	4,2	-1056	24	-1112	4	2,353	
Vinylics (all)			**6,6**	-1118	91	**-1270**	57	1,674	**76**
Acryl-Dispersion	3,3	0,7	**4,5**	191	64	**83**	39	1,690	**88**
Acryl-PSA1	3,5	0,2	to be determined individually	492	56	to be determined individually	6	2,015	
Acryl-PSA2	8,9	0,3		-188	32		4	2,353	

Table 3: "Upper bound" parameters for the estimation of diffusion coefficients in substrates

Substrate-Group	A_P' (mean)	SD (A_P' value)	upper-bound A_P'* value	τ (mean)	SD (τ)	upper-bound τ* value	n	student t (0,05, n-1, single sided)	Activation energy [kJ/mol]
Paper (from the test systems)	5,6	0,6	**6,6**	-1018	526	**-1902**	49	1,68	**71**
Cardboard (polar esters + BDGA)	3,0	0,6	**4,0**	-1247	85	-1391	33	1,70	74
Cardboard (hydrocarbons)	6,5	0,5	**7,4**	-1387	112	-1578	27	1,71	74
Cardboard (all)				-1310	120	**-1511**	60	1,67	**74**
PVC plast.	10,2	0,9	**12,8**	460	187	**-86**	3	2,92	
OPP	9,9	1,1	**11,8**	1595	40	**1527**	25	1,71	
LDPE	9,8	0,5	**10,8**	-77	47	**-172**	6	2,02	

The obtained "upper bound" diffusion parameters A_P'* and τ* can be used for estimation of diffusion coefficients in natural and synthetic rubber, vinylic (EVA, VAE, PVAC) type and acrylic dispersion adhesives. Furthermore for diffusion modelling in paper and paperboard apparent A_P'* and τ* values could be obtained from the net overall mass diffusion through the layers. The A_P'* and τ* values obtained for the plastic substrate layers fit to those in the EU modelling guide (PVC plast, 30% plasticiser A_P'* 14.6, τ* 0; OPP A_P'* 13.1, τ* 1577; LDPE A_P'* 11.5, τ* 0) . For verification the predicted migration values using these parameters were compared to experimental ones from 45 market samples and showed compliance or overestimation in 97% of cases (Aznar, M., P. Vera, et al. (2011): Journal of Materials Chemistry **21**(12): 4358-4370).

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