Mass Transfer in Thin Layers

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Abstract

Mass transfer and molecular diffusion in thin layers play an important role in many research fields. Examples include paints and varnishes, foils for LCD-panels, solar foils, transdermal patches, or medical test strips and membranes for liquid separations. The diffusion behavior has an important impact on the physical and chemical properties, including mechanical and optical properties, wetting behavior or drug release rates i.e. the product quality of the polymeric system. Precise experimental techniques for reliable measurements are key issues for further developments in this research field, especially with multi components. The experimental technique, which is used in the studies, is the Inverse-Micro-Raman-Spectroscopy (IMRS), which has been developed in a collaboration in Karlsruhe [1, 2]. Chemical compositions in multi-component mixtures can be detected locally and contact-free. Currently, concentration profiles in thin polymeric layers can be measured with a best level of temporal, spatial and quantitative resolution in this field. Extended and new experimental apparatus are constructed especially for precise measurement of multi-component diffusion under controlled boundary conditions. Experimental results will be used to evaluate and develop mathematical models for multi-component mass transport in collaboration with the research group of Richard Cairncross. In this contribution different applications of mass transfer in thin layers will be presented and a brief outlook on new experimental developments in this research field will be given.

1. Inverse-Micro-Raman-Spectroscopy
Construction and set-up of a new Micro-Raman-Sorption-Cell

Precise experimental techniques for reliable measurements are key issues for further developments in the research field of diffusion in polymeric thin layers. In Karlsruhe, in collaboration with a company a new measuring technique (IMRS) was developed [1], which combines a confocal Raman spectrometer and an inverse microscope.

Focus of the current research work is to investigate the influence of solvent mass flux in multi-component mixtures on the mass transfer mechanism of non-volatile species called "non-volatiles" e.g. additives like active agents or softeners (plasticizers) in polymeric systems. Experiments shall be performed at well defined solvent fluxes. In order to perform measurements under more precise controlled boundary conditions to measure diffusion processes in thin layers a Micro-Raman-Sorption-Cell is constructed based on the IMRS technique. This apparatus has the main advantage to adjust partial pressure of the pure solvents in a gas phase. Sorption and diffusion in thin layers can be measured in multi-component systems.

2. Calibration measurements of a multi-component (solvent-solvent-polymer) system

Raman Spectroscopy can selectively detect several chemical components in multi-component systems. This is demonstrated by calibration measurements of the ternary system poly(vinyl acetate)–toluene–methanol (polymer-solvent-solvent). Calibration measurements were performed and the results are shown in figure 1. In the diagram the intensity ratios of solvents per polymer are plotted against the solvent content of the sample. It shows clearly, that the measuring technique is suitable for investigation of multi-component polymeric system with more than one solvent and solute. Diffusion with multiple solvents will be investigated in a research project together with Richard Cairncross from Drexel University.

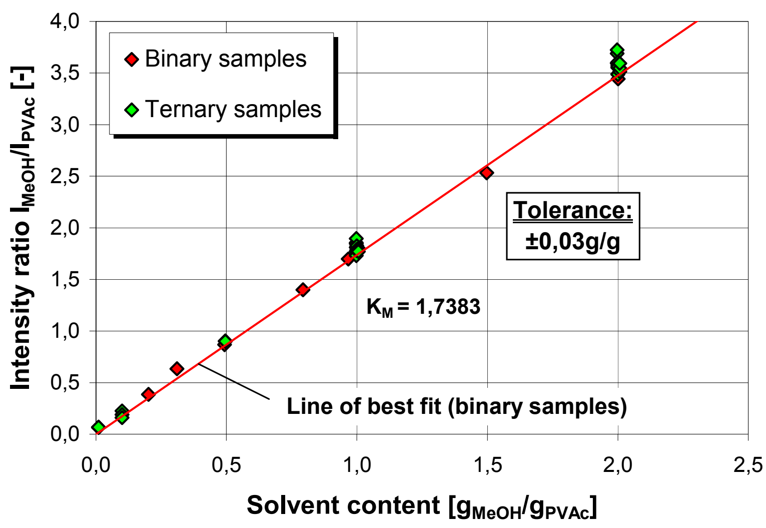

Figure 1 Calibration results with multicomponent solvent-solvent-polymer mixtures. (Methanol-Toluene-PVAc at different ternary compositions)

3. Preliminary measurements of non-volatile species (e.g. softener, drugs, additives) in multi-component polymeric systems

Raman depth profile measurements were performed on the final dried product still containing "non volatile species" e.g. transdermal patches. Transdermal patches represent an advanced technology of drug delivery. In transdermal patches of the so called 'next generation' there is no control membrane needed and the active agent is stored in a polymeric matrix. Drug release rates are directly controlled by the diffusion of the active agent ("non-volatile" species) in the polymer matrix. This design opens up new fields of application continuously and therefore new combinations of the required active agents and matrix polymers with almost unknown diffusion properties have to be developed. Additionally, the new applications require high accuracy of the active agent dosage in the matrix and the distribution in the patches. To meet these increasing requirements, better and more accurate experimental investigations are needed.
There are several applications of this drug delivery mechanism where the active agents have different diffusion properties that are still unknown. The influences of molecular size and polymer matrix mole mass have not been satisfactorily investigated yet. Transdermal patches of the "next generation" are likely to be produced through a casting process where the active agent is dissolved in a multi-component polymeric solvent mixture. In the final product (patch) the drug should remain homogeneously distributed in the polymer matrix. To design such a patch, the effect of evaporation rates on multi-component solvent and solute fluxes on the diffusion of non volatile species have to be taken into account. Existing theories will be used for this purpose or new model theories and diffusivity data for calculations will be developed in the research work in the next years.

Cellulose tri-acetate (CTAc) is a practically relevant polymer that has received much attention in the literature, yet the diffusion properties of CTAc are poorly understood. In industrial applications this polymer system is mainly used in the production of foils for LCD-panels. This LCD panel foil is produced in a casting process and the dissolved polymer solution is a multi-component mixture of CTA with the different solvents and different "non-volatile" species (additives, plasticizer). Experiments with this multi-component material system have been carried out with IMRS technique. Besides monitoring multiple solvents diffusion during the evaporation process, the focus of these investigations was, to measure the residual distribution and homogeneity of the solids in the final film. This is a key issue for the quality of products (especially for LCD foils) which has not been investigated in detail in the literature so far. Experiments were carried out with this technical multi-component system (mixtures of CTAc, softener and a solvent mixture of three solvents at different solvent fluxes (evaporation rates). Figure 2 shows the influence of the different solvent fluxes (evaporation rates) on the distribution of the non-volatile species (softener) in the polymer matrix. The light dots represent the softener content in the film, dried at "standard" conditions. On the left hand side (depth = 0 μm) is the position of the glass plate, and on the right hand side the surface of the dry film ($\approx$ 50 μm). This diagram clearly shows the inhomogeneous distribution of the softener content with a minimum slightly below the surface. These measured additive profiles led to the idea to influence their formation by changing the solvent flux (drying conditions). Therefore, preliminary experiments at called "gentle drying conditions" were performed and the results are shown as dark dots in figure 2. The results from these first measurements are very fascinating. It clearly reveals, that changing the solvent fluxes in this multi-component system leads to different mass transfer and influences the diffusion of the non-volatiles and hence the formation of the softener profile in the final film. Such profiles haven't been measured yet in this research field. Furthermore no way has been established to influence this distribution by means of changing the boundary conditions.

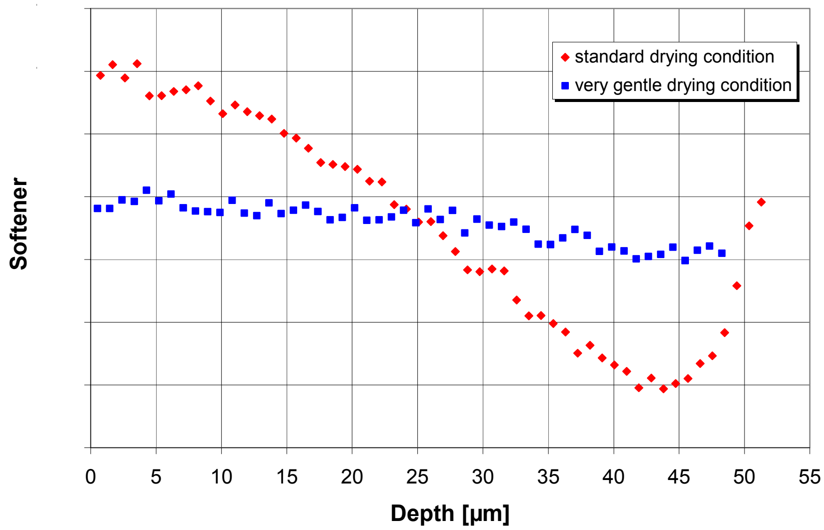

Figure 2: Influence of solvent flux in a multi-component system on the diffusion of non volatile (softener) in a polymer matrix (CTAc-foil for LCD panels). (The softener content is shown only qualitatively and in arbitrary units due to confidential restrictions)

This figure shows clearly the interaction of mass transfer mechanism in multi-component systems with volatile and non-volatile species. Especially for the industrial production of high quality products like LCD-panels (CTAc-foils) which are usually produced under "standard conditions". Such mass transfer interactions are not really known or even understood yet.

Diffusion phenomena shown in figure 2 cause undesired optical and mechanical properties in optical foils and are neither considered nor described by existing model theories yet. New model approaches and material data are necessary and will be one outcome of the future work.

[1] Schabel W, Scharfer P, Müller M., Ludwig I., Kind M., Raman Update Autumn 2005: Horiba Jobin Yvon, *Concentration Profile Measurements in Polimeric coatings during drying by means of Inverse-Micro-Raman-Spectroscopy (IMRS)*; 2005, No. 3, Page 1-3

[2] Schabel W., *Inverse Mikro Raman Spektroskopie - eine neue Messmethode zur Untersuchung lokaler Stofftransportvorgänge in dünnen Filmen, Folien und Membranen*; Chemie Ingenieur Technik, 2005, 77, No. 12, 1915-1926