



ELSEVIER

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: www.elsevier.com/locate/polytestPOLYMER
TESTING

Test Method

Simultaneous and time resolved investigation of diffusion processes of individual model fuel components in acrylonitrile-butadiene-rubber in the light of swelling phenomena


 Artur Blivernitz^{a,*}, Tobias Förster^b, Sebastian Eibl^b
^a *Institute of Mechanics, Universität der Bundeswehr München, Werner-Heisenberg-Weg 39, 85579, Neubiberg, Germany*
^b *Wehrwissenschaftliches Institut für Werk- und Betriebsstoffe, Institutsweg 1, 85435, Erding, Germany*

ARTICLE INFO

Keywords:

Diffusion
Elastomer swelling
Aviation fuels
Gas chromatography/Mass spectrometry
Sorption

ABSTRACT

This work introduces a method allowing a simultaneous and time resolved tracing of diffusion processes of individual components of model fuel mixtures in elastomers using gas chromatography/mass spectrometry (GC/MS). Uptakes of dodecane and m-xylene, representing typical fuel components, were monitored in acrylonitrile-butadiene-rubber (NBR) specimens, which were stored in different mixtures of these two compounds. Calculations of individual diffusion coefficients and saturation concentrations of each substance show rising uptakes and diffusion rates of both constituents with increasing m-xylene content of the mixture. Additionally, sorption curves of dodecane were recorded for elastomers, which were pre-swollen in m-xylene or decalin. At the same time, the extraction of the pre-swelling agents was traced. Diffusion coefficients of dodecane were significantly higher compared to those found for the neat material.

By immersing elastomers in binary mixtures containing different model fuel constituents, a relation between concentrations in the bulk fluid, individual swelling potentials of the mixtures' components and the attained equilibrium concentrations in the elastomer could be determined. In general, swelling potentials of mixtures are governed by the constituent with the highest individual swelling potential. Results from experiments involving model substances were interpreted in terms of the influence of a real fuels' composition on its swelling behavior towards elastomers contributing to a better understanding of diffusion processes.

1. Introduction

It is well known that elastomers in contact with various fluids, show swelling phenomena caused by an uptake of certain components of the liquid. In contrary, additives of the elastomer may be extracted during this process [1]. The velocities and extents of the occurring diffusion processes strongly depend on the composition of the surrounding liquid, the kind of additives and on the chemical constitution of the rubber. Swelling poses a serious challenge as mechanical properties of the elastomer can be affected in a negative way [2–4]. For in-service applications, it is therefore of major importance to select rubbers showing appropriate compatibility towards the surrounding fluid [5,6].

For example, aviation turbine fuels contain a large variety of different chemical components. The majority of the constituents belong to the substance classes paraffins, cycloalkanes (naphthenes) and aromatic hydrocarbons [7–9]. Depending on the concentration of individual components, physical properties of fuels like density, flashpoint, boiling point and especially the swelling potential may vary [10,11].

A common elastomer applied in contact to non-polar fluids is acrylonitrile-butadiene-rubber (NBR), due to its polarity, which is caused by nitrile groups [12]. However, e.g. fuels with high aromatics concentrations can cause a pronounced swelling of NBR materials, depending on their acrylonitrile content [11,13]. Therefore, understanding the influence of certain substance classes on the diffusion behavior is essential. Although various elastomers provide an even better resistance to non-polar liquids, NBR is the most important material for fuel carrying systems.

A large number of studies have been carried out to investigate the swelling behavior of NBR in various organic liquids [14–17]. Elastomer-specific structure parameters like filler type, crosslink density and mode of crosslinking were taken into consideration with regard to sorption processes [18–20]. In addition, also the influence of molecular properties as size, shape and polarity of the penetrating liquids, on the diffusion behavior was subject of research [21–23]. Nevertheless, concurrent sorption and extraction, as well as diffusion of individual components of a mixture, were not traced, as the performed

* Corresponding author.

E-mail addresses: artur.blivernitz@unibw.de (A. Blivernitz), Tobias1Foerster@Bundeswehr.org (T. Förster), SebastianEibl@Bundeswehr.org (S. Eibl).

gravimetric sorption experiments are not capable of providing data for both processes simultaneously. Apart from this, different analytical techniques, such as raman- and infrared spectroscopy as well as nuclear magnetic resonance, were used to study diffusion kinetics of fluids in polymers [24–26]. However, these methods require unique signals with adequate intensities of the investigated penetrant, which also do not overlap with signals of the polymer. Especially when single components of mixtures, consisting of similar compounds, are examined, signal overlaps may make the measurement impossible. A previous study has shown, that GC/MS assisted sorption experiments are able to cope with these challenges allowing not only quantification of sorbed penetrants but also investigations of diffusion kinetics [27].

Therefore, the emphasis of this work lays on a detailed description and quantification of diffusion processes for an in-service NBR with respect to the mass transport of individual substances representing typical aviation fuel components.

For this purpose, sorption experiments were carried out on NBR samples in different model liquids, whereby uptakes of the constituent components were traced simultaneously via gas chromatography/mass spectrometry (GC/MS). Additionally, a special focus was placed on the monitoring of concurrent sorption and extraction processes in pre-swollen elastomers to investigate the behavior of in-use materials. As the objective is to get a detailed and comprehensive understanding of fundamental interactions between elastomers, additives and fuels, the number of influential factors is kept to a minimum. Hence, model fuels are used instead of real aviation fuels to drastically reduce the amount of components and all experiments are carried out at room temperature with one elastomer.

Calculations of diffusion coefficients and saturation concentrations from sorption and extraction curves show that pre-swelling may reduce the resistance of the elastomer towards other solvents.

Results from the investigations of the model liquids are interpreted with regard to changes in a real fuels' swelling behavior with varying fluid composition.

2. Experimental

2.1. Materials and reagents

All experiments were carried out with a carbon black filled acrylonitrile-butadiene-rubber (NBR) with an acrylonitrile content of 18%, supplied by Deutsches Institut für Kautschuktechnologie (DIK). The detailed composition of the material is given in Table 1.

For most experiments, elastomer samples were extracted with acetone for 5 days in a soxhlet apparatus to completely remove the soluble additives DEHP, 6-PPD, stearic acid as well as residual CBS and TMTM-80. After extraction, specimens were stored in air for 2 days, until acetone was completely desorbed. Immersion mixtures and GC/MS-standard solutions were prepared by using analytical grade reagents, namely, decane, dodecane, hexadecane, decalin, m-xylene,

Table 1
Formulation of the investigated NBR elastomer.

Component	Content / phr
Perbunan 1846	100
Bis(2-ethylhexyl) phthalate (DEHP)	20
N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylene diamine (6-PPD)	2
Carbon black (type: N550)	60
Zinc oxide	5
Stearic acid	1
Sulfur	2
N-Cyclohexyl-2-benzothiazole sulfenamide (CBS)	1.5
TMTM-80 ^a	0.5

^a 80% tetramethylthiuram monosulfide, 20% elastomer binder and dispersing agents.

Table 2

Compositions of the six investigated binary mixtures. Combinations of Component 1 and 2: dodecane/decane, dodecane/hexadecane, dodecane/decalin, mesitylene/cumene, dodecane/1-methylnaphthalene, dodecane/mesitylene.

Component 2 concentration / mol-%	Component 1 concentration / mol-%
9	91
20	80
33	67
50	50
77	23

mesitylene, cumene, tetralin, 1-methylnaphthalene and n-heptane (> 99%, Sigma Aldrich).

2.2. Instrumentation

An Agilent 7890 A gas chromatograph coupled with an Agilent 5975 MSD mass spectrometer was used to perform GC/MS analyses. The column was a 30 m DB-5MS (0.25 mm inner diameter, 0.25 μ m film thickness). Weighing processes were carried out with an analytical balance AG 285, supplied by Mettler Toledo (accuracy: \pm 0.01 mg).

2.3. Equilibrium swelling experiments with binary mixtures

Small cylindrical elastomer pieces (ca. 3–6 mg), which were extracted with acetone, were placed in 5 ml screw-tight vessels containing model mixtures, consisting of two different substances, after their initial mass (m_0) was determined by weighing. The compositions of these liquids are listed in Table 2.

Based on preliminary studies the storage time was conservatively defined as 7 days to ensure that equilibrium swelling was reached. Afterwards, the specimens were taken out and cleaned with benzene. It was taken special care to keep the time of contact between samples and benzene under 1 s to ensure that extraction of absorbed components could be considered negligible. In order to finally extract the sorbed substances, the elastomer pieces were placed in GC-vials and 1 ml of n-heptane was added. After extraction was completed the solutions were analyzed via GC/MS. From results of pretests, extraction time was conservatively determined as 2 days. Quantification of each constituent was performed by external calibration. For this purpose 5 standard solutions, containing the investigated components in appropriate concentration ranges, were analyzed by GC/MS and linear calibration curves were calculated to determine the masses of the sorbed substances. The saturation concentrations of the components were then calculated as the substance mass in the equilibrium state (M_∞) divided by the mass of the extracted elastomer (m_0). As proven by a previous work, the described GC/MS assisted methodology provides reliable results, which are in good accordance with gravimetric measurements [27].

2.4. Time resolved sorption experiments with mixtures of m-xylene and dodecane

To enable a simplified, one-dimensional consideration of diffusion, thin elastomer sheets ($30 \times 10 \times 1 \text{ mm}^3$), which were extracted with acetone, were stored in 60 ml screw-tight glass vessels containing mixtures of m-xylene and dodecane with different concentrations (see Table 3). After different times, the specimens were taken out and cleaned with benzene. Each time a small piece (ca. 3–6 mg) was cut out of the elastomer sheet, weighted and placed in a GC vial. Pieces were removed in appropriate distances from already generated holes and specimen edges to make sure that diffusion was only considered in one dimension. Extraction and quantification of sorbed substances were performed analogue to chapter 2.3. Fig. 1 exemplarily shows the

Download English Version:

<https://daneshyari.com/en/article/7824299>

Download Persian Version:

<https://daneshyari.com/article/7824299>

[Daneshyari.com](https://daneshyari.com)