

Transport Process of Fuel Components through Elastomer Micro- and Nano- Composites

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Devoted to my beloved mum

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"The Volatile Organic Substance Permeability of Nano- and Micro-Rubber Composites"

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Abstrakt

Die vorliegende Arbeit beschäftigt sich in einer detaillierten wissenschaftlichen Studie mit der Diffusion und Permeation von niedermolekularen, flüchtigen, organischen Substanz durch Kautschukelastomere, bzw. durch mit mikro- und nanoteilige Materialien gefüllte Elastomercomposits.

Als Modellsubstanz für solche organischen Verbindungen wurde in dieser Studie *tert*-Butylbenzol gewählt. Zu seiner quantitativen Bestimmung wurden zwei Testmethoden bevorzugt angewandt. Eine eigens hierfür entwickelte und gebaute Zweikammerpermeationsapparatur wurde hauptsächlich für die Untersuchungen der Diffusion und Permeation verwendet. Als Referenzmethode zur Überprüfung und Korrelation der genannten Permeationsapparatur diente die ATR-FT-IR Spektroskopie.

Verschiedene Elastomertypen, die sich in ihrer Molekularstruktur und ihren chemischen Eigenschaften unterscheiden (BR, SBR, EPDM, NBR, HNBR), wurden zunächst untersucht. Hierbei wurde der Einfluss der Polymerkonstitution, des `freien Volumens`, der Polarität, der Kettenbeweglichkeit und der Vernetzungsdichte auf das Diffusions- und Permeationsverhalten von *tert*-Butylbenzol systematisch ermittelt und ausgewertet.

Für die Herstellung der Composites wurden zwei relativ polare Elastomere - NBR und HNBR - als Kautschukmatrix gewählt. Vier verschiedene Typen von Füllstoffen – Russ, Silica, Schichtsilikat und Mikroglasplättchen –, die sich durch Form (kugel- oder plättchenförmig) und Größe (mikro- oder nanoteilig) unterscheiden, wurden in die Polymermatrix unter Verwendung verschiedener Mischverfahren (Mechanisches Mischen, Co-Koagulation, etc.) eingearbeitet. Der Einfluss der Füllstoffmorphologie, des Füllstoffgehaltes, der Füllstoffverteilung, der Polymer / Füllstoffwechselwirkung sowie der Mischmethode wurden intensiv untersucht.

Ermittelt wurden auch die mechanischen Eigenschaften der Composites, wie z.B. das Zug / Dehnungsverhalten und die dynamisch mechanischen Eigenschaften, welche eine wichtige Bedeutung in der industriellen Anwendung besitzen.

Schlüsselworte: Diffusion, Permeation, Füllstoffmorphologie

Abstract

This current dissertation is focused on the investigation of the diffusion and permeation properties of low molecule volatile organic substance through elastomer and its micro- and nano- composites. The *tert*-butyl-benzene (t-BuPh) was used as model substance in the study.

In order to carry out the investigation quantitatively, two test methods were applied. An in-house developed and self-constructed two-chamber permeation apparatus was used mainly for the diffusion and permeation measurements. The ATR-FT-IR spectroscopy was utilized as a reference method to examine and correlate the two-chamber permeation method.

Several different kinds of neat elastomers containing varying molecular structures and chemical properties – BR, SBR, EPDM, NBR, and HNBR – were investigated as first. The influence of the polymer constitution, the “free-volume”, the polarity, the chain flexibility, and the elastomer cross linking density on the diffusion and permeation behavior of t-BuPh was studied and evaluated systematically.

For the composites preparation, two kinds of relative polar elastomers – NBR and HNBR – were chosen as polymer matrix. Four types of fillers – carbon black, silica, layered silicate, and micro glass flake – possessing varying shape (spherical or plate-like) and size (micro or nano) were mixed into the polymer matrix by using different processing methods (mechanical mixing, chemical co-coagulation, etc.). In this case, the influence of filler morphology, filler content, filler distribution, polymer-filler interaction, and mixing method of filler on the diffusion and permeation properties of the composites was investigated intensively.

The mechanical properties of the composites, e.g. strain stress behavior, dynamic mechanical property, which possess important meaning for the industrial application, were also studied as well.

Key words: Diffusion, Permeation, Filler-morphology

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1 Introduction

The rapid development and widespread application of polymeric materials in various areas such as sealings, membranes, fuel and fluid systems, tire inner liners, bins, beverage containers, packaging etc. have created considerable interest in new materials with very low permeability but at the same time good mechanical performance and durability under severe service conditions [1]. An important environmental and technical demand is to fulfill actual regulations especially in the automotive industry, e.g., on the subject of "zero emission vehicle" [2]. This subject is important because an elastomer is always used in contact with foreign substances which may be gases or liquids that can migrate into or out from it. This starts already in the manufacturing stage and continues when the finished products are in contact with gases such as oxygen or with liquids, lubricants, gasoline and other fuels. Furthermore, it should be taken into account that some additives in modern fuels may affect the permeability of various polymers [3], which can result in higher fuel emissions. The search for materials with low permeability for gases and liquids is paralleled by the effort to better understand and predict the transport process of such substances through polymer membranes.

Associated with the problem of minimizing fuel permeation is a deeper knowledge of molecular parameters and interactions that have an influence on the kinetics of diffusion and the mass transport of low molecular weight constituents in polymer matrices [4, 5]. The diffusive transport and the sorption of the penetrant (diffusant) molecules in the polymer matrix contribute to permeation. A fruitful group of concepts to understand and predict the diffusive transport in polymers exploits the idea that "holes" or "free volume" existing on a molecular level facilitate not only the mobility of the polymer translational modes but also the translational movement of the diffusant [5]. Because the "free volume" changes significantly at the glass transition temperature, the transport process in glassy thermoplastic materials is much more reduced than in amorphous rubbery materials. Elastomeric materials formed by cross-linking of rubbers above T_g demonstrate a considerably higher amount of "free volume" and facilitate the diffusive transport of gases and liquids as a consequence [5]. However, due to their outstanding elastic properties, elastomeric parts made from cross-linked rubber are used in the majority of dynamic applications in automotive, aerospace, oil well and other high-performance applications. Therefore, the development of elastomers with high permeation resistance for gases or liquids is still a challenging task, because any improvements in the permeation resistance should not affect the mechanical and wear and tear performance of the elastomeric parts.

One concept to overcome this complex problem is to select tailor-made polymers with an adequate chain architecture that reduces the "free volume" and a defined polarity in order to prevent sorption and swelling of the diffusant molecules in the ma-

trix. Special rubbers with a maximum amount of short side groups along the main chain, like poly-isobutylene or with polar chain units, like poly(butadiene-co-acrylonitrile), poly-acrylates, fluorinated rubbers have been synthesized and are widely used for these challenging applications [6, 7]. However, compared to thermoplastic materials, the published literature concerning permeation gases and liquids in elastomers is rather limited. Therefore a more detailed and systematic knowledge about the influence of molecular parameters is highly awarded.

Investigations have been focused on mainly the influence of the rubber grade on solvent uptake under technological relevant conditions. Structure property relationships for the influence of the polymer nature and permeate molecular structure and size [6, 8-11] and the rubber's cross-link density have been established [12]. It was demonstrated that the diffusion coefficient of gases and low molecular weight liquids scales inverse proportionally to its molecular weight and the viscosity of the matrix polymer [6, 11, 13]. Even so, it is still not certain if the activation energy of the diffusion process scales with the diameter of the permeate molecule d or with the square d^2 [14, 15]. A quite intensive work was focused on the incompatibility between the polymers and permeates [6]. The kinetics of swelling of NBR and HNBR have been investigated in aromatic oils and alternative fuels with regard to oil field and automotive applications [20]. However, a systematic investigation of the diffusive transport of fuel constituents in related polar polymers like NBR and HNBR as a function of (i) the acrylonitrile content, (ii) the main chain un-saturation, and (iii) the cross-link density has not been performed until now.

Another concept to improve the permeation resistance is that of physically blending two polymers. Even if the blending technology provides such materials rapidly and economically, the properties of the gas or liquid transport properties depend mainly on the chemical nature of the continuous phase [13]. However, this approach suffers because the size and the shape of the domains with reduced "free volume" are strongly dependent on processing parameters.

The third and most efficient approach to reduce the permeability of gases and liquids through polymers is to incorporate and disperse non-permeable plate-like fillers into the polymer matrix. At constant filler volume fraction, the diffusion path becomes more tortuous if the filler dispersion is better and the aspect ratio is higher [6]. In addition, physically absorbed polymer layers on the filler surface should also reduce the diffusive transport. This aspect was rarely considered in experimental investigations. A comparison between plate-like and iso-dimensional fillers (i.e. carbon black and precipitated silica) revealed for the latter rather unsatisfactory barrier properties [6, 7].

In recent years, the search for more efficient barrier properties and high reinforcing effects was geared in particular to natural or synthetic layered silicates (i.e. montmorillonite, saponite, hectorite) [17]. Their potential as permeation barriers is inherent

in their crystal structure, which is interesting in its own right [18, 19]. Nano-composites of polar thermoplastic materials (i.e. polyamide, poly-vinyl alcohol, polyethylene oxide) and organically modified smectites (organo-clays) have been prepared by solution intercalation of monomers and subsequent polymerization or solution blending with polymers and demonstrate efficient barrier properties at far less volume fractions than iso-dimensional fillers [17]. However, the dispersion and orientation of pristine layered silicates and organically modified clays into hydrophobic polymers like polypropylene and high molecular weight rubber like NR, SBR, EPDM, NBR is still an challenging target. While improvements in mechanical properties become evident [20] the full potential of clay to enhance the barrier properties could not be established because of poor dispersion properties.

To overcome problems in the preparation of rubber/clay nano-composites, new techniques such as the "static latex compounding" (SLC) [21, 22] and the "continuous dynamic latex compounding" (CDLC) [23] have been developed. There are serious references that these unconventional mixing techniques lead not only to a significant decrease of permeability but also to an efficient mechanical reinforcement at very low filler volume fractions. Besides plate-like fillers, also micron-sized inorganic flakes such as mica [32] and glass [33] have been tested in a few rubbers, while taking advantage of the rather simple mechanical incorporation of these fillers.

More systematic measurements are required to clarify the effects of inorganic particles on permeation. For example, to establish permeability measurements for samples containing the same matrix with different types of inorganic particles or different matrices with the same dispersed particles. It can be foreseen that the interest in clay/rubber nano-composites will be fueled mostly by anisotropic effects on mechanical properties and barrier functionalities that could be achieved by efficiently exfoliated clays.

Although the driving applications for these materials are quite obvious, the theoretical modeling of permeability through nano-composites is still developing. The theoretical models predict the fluid permeability as a function of the volume fraction, the aspect ratio, size and size distribution and orientation of the filler particles [26]. However, limitations arise from the lack of information about the shape, size and orientation of the positional distribution of the plates in the real nano-composites.