



Photo-patterned natural rubber surfaces with tunable tribological properties

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ABSTRACT

The present work highlights the use of UV induced thiol–ene click chemistry for designing elastomer surfaces with tailored friction properties. A two-step surface modification strategy based on two consecutive photoinduced thiol–ene reactions has been developed which enables controlled and patterned immobilization of micro-scaled inorganic particles onto diene–rubber surfaces. The influence of the coupled particles on both surface topography and surface roughness is determined by microscopic techniques whilst tribological studies are carried out to characterize the friction properties. The results give evidence that the attachment of selected micro-scaled particles provides a distinctive increase in surface roughness and a considerable decrease in the coefficient of friction. Both are influenced by the amount of particles immobilized onto the elastomer surface. The application of photolithographic techniques further provides elastomer materials with precisely and spatially controlled tribological properties. Whilst elastomer surfaces with randomly attached particles exhibit isotropic coefficients of friction, the tribological properties of micro-patterned elastomers are anisotropic.

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1. Introduction

Along with their ability of attaining desired specific material properties, surface functionalization techniques offer a versatile way to obtain elastomer types with new functionalities, and play a key role in numerous fields of application ranging from the automobile industry to the health-care sector [1–3].

In particular, controlled surface chemistry and topology are crucial when it comes to the tribological characteristics of elastomer materials as they strongly govern the interaction between material surfaces in contact. Common

approaches that aim at the development of new elastomer articles with improved wear-resistance, extended service life or reduced friction properties pursue chemical as well as physical surface modification routes [4]. State-of-the-art chemical techniques involve the irradiation of elastomer surfaces with high energy radiation leading to an increase in surface hardness due to post-crosslink reactions. Another strategy utilizes the attachment of thin organic layers such as molecular layers onto rubber substrates to achieve tailored tribological properties [5,6]. In addition, plasma techniques in the presence of fluorine components including SF₆ or CF₄, as well as fluorination with reactive fluorine gas mixtures are often employed to attach fluorine moieties onto elastomer surfaces. Although fluorinated elastomer surfaces are characterized by reduced surface friction and enhanced wear-resistance, account has to be

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taken into the fact that they suffer from poor wettability by lubricants due to their low surface energy [7–9].

In terms of physical techniques, recent work has focused on the application of coatings onto elastomer surfaces via sol–gel processes using SiO_2 and other selected inorganic nano-scaled particles (e.g. Al_2O_3) that impart reduced surface friction [10]. Over the last years significant effort has been expended toward the deposition of thin coatings of amorphous diamond-like carbon (DLC) onto elastomers that lead to an increase in surface roughness at nanometer and micrometer scales and a significant decrease in the coefficient of friction (COF) [11,12]. However, these methods are not without shortcomings since the insufficient adhesion between the hard inorganic layer and the soft and flexible elastomer matrix often limits stable friction properties during service life [13].

Whilst the intent is often to provide uniform surface functionalization, nano- and micro-patterning techniques have gained increased attention in the controlled tuning of frictional and adhesive properties at solid/solid and solid/liquid interfaces. Most of the employed patterns are directly inspired by natural surfaces such as the fibrillar structure of gecko feet, the aligned riblet structures of shark skin or the randomly distributed convex nano-asperities of lotus leaves [14–17]. Typical surface texture techniques rely on directional chemical etching, focused ion beam sputtering and selective removal of materials by laser ablation and micro-abrasion. With respect to biomimetic surfaces, soft-lithography has become a popular technique to generate micro-scaled patterns onto soft elastomer materials particularly based on polydimethyl siloxane [18–24].

The present work aims at the controlled functionalization of diene-elastomer surfaces by UV induced thiol–ene click chemistry which offers a new approach toward patterned elastomer surfaces with tunable friction properties. Classical UV initiated thiol–ene reactions follow a free-radical mechanism and can be initiated by numerous uni- and bimolecular photoinitiators. The excitation of the photoinitiator leads to a formation of free photoinitiator radicals that can abstract hydrogen from the relatively weak hydrogen–sulfur bonds of thiols. The addition of the formed thiyl radicals to both electron rich and electron poor $\text{C}=\text{C}$ double bonds displays the unique features of click reactions among them high yields, ambient process conditions, high reaction rates and insensitivity to water and oxygen [25]. Due to its versatility, highly efficient thiol–ene click chemistry has become implemented in numerous technologies that range from photopolymerization and photolithography to polymer functionalization strategies [26–28]. In addition, radical-mediated thiol–ene reactions together with catalyzed thiol–Michael reactions are widely used in “grafting to” and “grafting from” surface modifications of different types of polymer materials [29–31]. In particular, electron-deficient olefins such as functional acrylates are prominently employed in thiol–ene graft reactions in order to introduce new functionalities onto polymer surfaces among them improved adhesion, none-fouling or physiologically-active surfaces [32–35].

The photochemical approach provides a unique opportunity to adjust the tribological properties of an otherwise slip-resistant elastomer by lithographic techniques.

2. Experimental part

2.1. Materials

Natural concentrated rubber latex (high ammonia, 60 wt.% dry rubber content) was used as diene-elastomer substrate and was purchased from a Malaysian supplier. The photoinitiator ethyl 2,4,6-trimethylbenzoylphenylphosphine (Lucirin TPO-L) was supplied by BASF (Ludwigshafen, Germany). Trimethylolpropane tris(3-mercaptopropionate) (TriThiol) as poly-functional thiol was obtained from Bruno Bock Thiochemicals (Marschacht, Germany) and micro-scaled silica particles ($d_{50} = 2 \mu\text{m}$) functionalized with (3-vinylpropyl)-trimethoxysilane (Aktisil VM 56) were from Hoffmann Minerals (Neuburg, Germany). All other reagents were supplied by Sigma–Aldrich (St. Louis, United States) and were used without further purification. Lorica® Soft, a polyamide micro fiber fleece coated with polyurethane, was obtained by Ehrlich-Leder (Biberach, Germany).

2.2. Sample preparation

Natural rubber (NR) latex was pre-vulcanized using a UV assisted curing protocol based on radical-mediated thiol–ene click chemistry [36,37]. Solid films were prepared from this cross-linked latex using a coagulant dipping process. Porcelain formers were cleaned with acid and alkaline solutions and were then placed in an aqueous coagulant bath with calcium salts as coagulant and calcium carbonate as release agent. After a drying step the formers were immersed in the pre-cured NR latex. The dipped latex films were dried at 120°C for 15 min and films were obtained with a thickness ranging from 200 to $300 \mu\text{m}$. The films were cut from the formers using a scalpel and placed in petri dishes separately.

2.3. Photochemical attachment of functional thiols

The crosslinked NR films were placed in an emulsion containing 1.0 wt.% Lucirin TPO-L, 10.0 wt.% TriThiol and 1.1 wt.% Tween 20 in deionized water at 21°C for 10 min. After a drying step at 100°C for 1 min the samples were irradiated under nitrogen using a conventional Hg UV lamp (light hammer 6 UV curing system, Fusion UV Systems, United States). The exposure dose amounted to $6.3 \text{ J}/\text{cm}^2$ with a wavelength range between 240 and 460 nm as no light filter was employed. The light intensity into the sample plane was determined with an integrating radiometer (Powerpuck II, EIT Instrument Markets, United States) while qualitative spectra were measured with a spectroradiometer (Solascope 2000TM, Solatell, United Kingdom). The irradiated samples were rinsed with ethanol and water and dried again at 100°C for 10 min.

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