Photo-vulcanization using thiol-ene chemistry: Film formation, morphology and network characteristics of UV crosslinked rubber latices

Sandra Schlögl a, *, Marie-Luise Trutschel b, Walter Chasse b, Ilse Letofsky-Papst c, Raimund Schaller d, Armin Holzner d, Gisbert Riess e, Wolfgang Kern e, Kay Saalwächter b

a Polymer Competence Center Leoben GmbH, Roseggerstraße 12, A-8700 Leoben, Austria
b Institut für Physik – NMR, Martin-Luther-Universität Halle-Wittenberg, Betty-Heimann-Straße 7, D-06120 Halle, Germany
c Institute for Electron Microscopy, Graz University of Technology, Steyrergasse 17, A-8010 Graz, Austria
d Semperit Technische Produkte GmbH, Triester Bundesstraße 26, A-2632 Wimplingen, Austria
e Chair of Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, A-8700 Leoben, Austria

Article info
Article history:
Received 8 April 2014
Received in revised form 1 June 2014
Accepted 3 June 2014
Available online 10 June 2014

Keywords:
Diene-rubber latex
Film formation
Thiol-ene chemistry

Abstract
The photo-vulcanization with versatile thiol-ene chemistry represents an innovative approach to crosslink diene-rubber materials both in latex and in solid film state. In this work, the structure of elastomer-based thiol-ene networks and the morphology after film formation are studied in detail using electron microscopic techniques, atomic force microscopy and multiple-quantum solid-state NMR spectroscopy. Additionally, film formation properties and corresponding macroscopic properties of photo-vulcanized natural rubber (NR) latex and its synthetic counterpart, isoprene rubber (IR) latex, are determined in dependence on the curing procedure (pre- and post-vulcanization). The results reveal that thiol-ene cured elastomers comprise homogenously distributed crosslinks with a low amount of short chain defects. Whilst photochemically pre-cured NR latex particles provide coherent films, the film formation and mechanical properties of IR are strongly governed by the crosslink density of the latex particles. In film state, photo-vulcanization promotes narrow crosslink distributions and excellent tensile properties of both NR and IR.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Although earliest reports on thiol-ene chemistry date back to 1905, the publications of Morgan and Ketley on photo-polymerization of thiol-ene monomers have become the starting point for extensive studies and widespread applications of thiolenes in the 1970s [1,2]. The photoinduced addition of thiols across unsaturated C=C double bonds follows a free radical mechanism where in the first step thiol radicals are formed by a hydrogen abstraction from photoinitiator radicals. The subsequent addition of the thiol radical to the alkene double bond creates a carbon centered radical. This radical can abstract a hydrogen from another thiol group leading to a perpetuation of the chain process in photopolymerization reactions [3,4]. Besides photopolymerization, UV induced thiol-ene chemistry is widely used in surface functionalization techniques, fabrication of polymer brushes, photo-lithography and modification of polymer materials [5–7].

Apart from the photoinitiated free-radical addition of thiols to electron-rich and electron-deficient alkenes, radical-mediated thiol-ene reactions can also be initiated by thermal initiators such as peroxides or 2,2′-azobis(isobutyronitrile). Thermal initiators are often used for large-scale synthesis as an uniform generation of radicals in large volumes can be easily achieved at elevated temperature [4]. The employment of thermally sensitive radical initiators has also recently gained increased attention in the functionalization of 1,2-poly(butadiene) and related copolymers via both thermally and photoinitiated thiol-ene chemistry. They have demonstrated that the selected attachment of functional thiols makes the preparation of stimuli-responsive copolymers with tailored physical and chemical properties feasible [10–12].
Account has to be taken into the fact, that not only radical-mediated thiol-ene reactions but also catalyzed Michael addition reactions carry salient features of click reactions which include high efficiency, rapid reaction rates, mild process conditions and high yields. The thiol-Michael addition is a catalyzed reaction between thiols and alkenes comprising electron withdrawing groups among them (meth)acrylates, acrylonitrile, maleimides or α,β-unsaturated ketones. Numerous catalysts ranging from strong bases and Lewis acids to nucleophilic amines and alkyl phosphines can be used to initiate the thiol-Michael reaction [4,13]. Due to its short reaction times under ambient conditions and its insensitivity to the presence of water and oxygen, the thiol-Michael reaction is particularly applied in the preparation of hydrogels and biomaterials [14,15].

In our work we have recently highlighted that versatile and unique UV induced thiol-ene chemistry can be employed to photo-vulcanize diene-rubber materials in liquid and solid state (see Scheme 1). Although side chain enes on the investigated diene-rubbers provide a higher reactivity than the C=C groups of the main chain, cis-1,4-poly(isoprene) rubber materials can be cross-linked successfully with crosslink yields comparable to sulfur cured materials [16]. Whilst the photo-vulcanization in solid state can be accomplished easily by a UV irradiation of the rubber films, the photo-vulcanization in latex state requires a homogenous illumination of thin liquid films (layer thickness below 1 mm) since latex emulsions exhibit a lower light transmissivity. In a new approach we have developed a continuous pre-vulcanization process using a falling film photoreactor to ensure a homogenous UV illumination of liquid latex formulations in thin films [17,18].

It should be noted that thermally initiated thiol-ene reactions allow a more flexible reactor design since they are not limited by light attenuation. However, our study focuses on UV induced thiol-ene chemistry as photochemical reactions provide desirable features when it comes to the large-scale vulcanization of diene-rubber latices. The energy consumption of the pre-vulcanization process can be reduced significantly because the UV induced crosslinking proceeds at room temperature. In addition, the design of the falling film photoreactor establishes a new way for continuous pre-vulcanization processes whilst thermally induced pre-vulcanization techniques are typically carried out in discontinuous processes [17,19].

The pre-vulcanization of rubber latices plays an important part in the enhancement of tensile properties and aging stabilities of thin film dipped latex goods [19]. On industrial scale processes the pre-vulcanization is usually carried out in the presence of sulfur or sulfur-donor agents. In addition, accelerators and activators are required that reduce the reaction time and reaction temperature [20]. Other thermal crosslinking processes involve the curing with peroxides or hydroperoxides whilst the curing with high energy radiation such as e-beam or gamma rays has become a well-established technique to produce pre-cured NR latex in pilot plant quantities [21–23].

Besides the mechanical properties, the film formation properties are directly affected by the employed pre-curing system. Recent work has revealed that sulfur pre-vulcanization as well as gamma-ray induced pre-curing of natural rubber (NR) latex leads to uniformly crosslinked rubber particles [24–26]. With respect to peroxide curing, only small NR particles exhibit a homogenous crosslink structure whereas a core–shell structure has been observed for larger particles [26,27]. The film formation of both natural and synthetic latices has been studied in detail and research has demonstrated that the film formation of polymer emulsions takes place in three major stages [28–30]. The first step involves the drying of the latex due to the evaporation of water from the latex surface. The evaporation rate is affected by various parameters such as the particle size, the chemical composition and stabilization of the latex or the glass transition temperature [31]. A concentration of the rubber particles takes place leading to the second step in which the latex particles come in contact and stick

![Scheme 1. Photo-vulcanization of diene-rubbers in liquid and solid state using thiol-ene chemistry.](image-url)
together irreversibly. In dependence on the hardness of the particles, deformation and coalescence are observed. Various theories involving wet-sintering and dry-sintering processes or interparticle cohesion promoted by surface forces have been proposed to explain the formation of ordered particle structures during this step [32–34]. In the last stage, the cores of the latex particles penetrate and the soft latex film obtains its mechanical properties (wet gel strength). In terms of highly pre-vulcanized latex particles or particles with a highly crosslinked shell structure, the polymer diffusion across particle boundaries is reduced or hindered due to the restricted mobility of the macromolecules chains [35]. As the macroscopic properties of the dried latex film are directly related to a coherent and efficient film formation it has to be considered that a balance has to be found between pre-vulcanization, film formation and mechanical properties of the final latex articles [29].

The present study focuses on the crosslink structure of elastomer-based thiol-ene networks and its influence on film formation properties, film morphologies and corresponding tensile properties of diene-rubber materials. In particular, this work addresses the network characteristics of thiol-ene natural rubber (NR) latex and its synthetic counterpart isoprene rubber (IR) latex. The photo-vulcanization is carried out in liquid state (pre-vulcanization of the emulsion) as well as solid state (post-vulcanization of solid films) and the effect of both procedures on the microscopic and macroscopic properties is determined in detail. Real time FT-IR spectroscopy is employed to investigate the reaction kinetics whilst the morphology of the photo-vulcanized elastomer films is characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM). Both multiple-quantum (MQ) solid-state NMR spectroscopy and equilibrium swelling measurements are used to obtain quantitative information on the network structure after film formation, as studied previously with a focus on entanglement effects [36,37]. In addition the corresponding mechanical properties, in particular the tensile strength, are measured by tensile tests. The correlation between crosslink structure, film morphology and macroscopic properties gives new insights into the characteristics of elastomer-based thiol-ene networks. Furthermore, crucial process parameters in photochemical pre- and post-vulcanization procedures are highlighted that considerably influence film formation and corresponding tensile properties.

2. Experimental part

2.1. Materials and chemicals

Natural concentrated rubber latex (high ammonia, 60 wt.-% dry rubber content) was purchased from a Malaysian supplier. Synthetic isoprene rubber latex (Kraton® IR0401 BU) with a dry rubber content of 63 wt.-% and a molecular weight ranging from 1,500,000 to 2,500,000 g/mol was obtained from Kraton Polymers (Amsterdam, The Netherlands). Ethyl 2,4,6-trimethylbenzoylphenylphosphinate (Lucirin TPO L) was provided by BASF (Ludwigshafen, Germany) and trimethylolpropane tris(3-mercaptopropionate) (TriThiol) was supplied by Bruno Bock Thiochemicals (Marschacht, Germany). All other reagents were from Sigma–Aldrich (St. Louis, United States) and were used without further purification.

2.2. Photo-vulcanization of NR and IR in latex state

In the first step of the UV pre-curing, 1.0 phr (parts per hundred parts of rubber) Lucirin TPO L and 1.0 phr TriThiol were emulsified in 2.0 phr deionized water. The emulsion of the photoinitiator and the thiol was added to 10.0 kg IR and NR latex, respectively, with a dry rubber content of 40 wt.-%. This latex mixture was stirred at room temperature by means of a magnetic agitator for 2 h. The pre-vulcanization of NR and IR latex mixtures was carried out in a falling film photoreactor using the same process parameters.

The scheme of the falling film reactor which was tailor made is depicted in Fig. 1. The reactor tube with an inner diameter of 135 mm was made of glass and contained an inlet for the latex mixture at the top and an outlet at the bottom. In the reactor tube a medium pressure Hg lamp (Heraeus) equipped with a quartz cooling tube was positioned centrically. The UV lamp comprised an arc length of 25 cm and was flooded with inert gas (nitrogen) to extend the longevity of the UV system. The latex mixtures were pumped continuously from a storage vessel to the top of the falling film reactor using an eccentric screw pump with a flow rate of 1.3 L/min. With these process parameters continuous and stable liquid falling films could be achieved with a film thickness in the range of 0.5 and 1.0 mm. The UV assisted pre-vulcanization was performed with a lamp power of 800 and 3000 W corresponding to a light intensity of 0.4 and 0.9 W/cm² (wavelength range between 240 and 460 nm), respectively. After each illumination cycle samples were taken and 0.5 phr Ionom LC as antioxidant was added to the pre-cured latices.

2.3. Preparation of solid latex films

A conventional coagulant dipping process was employed to prepare solid films from either non crosslinked or pre-cured diene-rubber latices. In the first step porcelain formers were cleaned with acid and alkaline solutions and placed in a coagulant solution containing calcium salts (coagulant), calcium carbonate (release agent) and surfactants. The formers were dried for 60 s at 120 °C, immersed in the various latex formulations for 30 s and dried again at 120 °C for 20 min. The thickness of the dried latex films was between 200 and 300 μm.
2.4. Photo-vulcanization of NR and IR in film state

An emulsion with 1.0 phr Lucirin TPO L and 1.0 phr TriThiol in 2.0 phr deionized water was added to NR and IR latex with a dry rubber content of 40 wt.-%. After adding 0.5 phr Ionom LC, the latex mixture was stirred at room temperature for 2 h and then solid films were prepared by the dipping process. These films were UV illuminated with a medium pressure Hg lamp (Hereaus) employing an exposure dose between 1.0 and 7.5 J/cm² (wavelength range from 240 to 460 nm). The UV irradiation was carried out under inert conditions to avoid any photo-oxidation effects on the elastomer surface.

2.5. Characterization of the crosslink kinetics

Real time FT-IR measurements were carried out with a large angle reflectance infrared (IR) cell (Perkin Elmer). The rubber samples were irradiated with a UV spot curing unit (Efos Novacure high pressure Hg emitter with a wave length range between 290 and 410 nm). IR spectra were taken with an FT-IR spectrometer (Spectrum One, Perkin Elmer) and the absorption peak areas were calculated with Spectrum 3.02 and Spectrum TimeBase 1.1 software. Sample preparation: 2 wt.-% rubber was dissolved in toluene and Lucirin TPO L and TriThiol were added to the solution. The concentration of the photoinitiator and thiol is stated in the discussion section. The solution was stirred for 15 min at room temperature by means of a magnetic agitator and then spin cast (4000 rpm, 20 s) on gold substrates. Each sample was fixed on a specimen holder in the large angle reflectance IR cell and the cell was flooded with inert gas for 10 min to avoid photo-oxidation during UV irradiation. The crosslinking via thiol-ene reaction was monitored during UV irradiation (1.1 W/cm² light intensity) by taking FT-IR spectra after various irradiation times. The light intensity into the sample plane was determined with a spectroradiometer (Solatell, Solascope 2000™).

2.6. Characterization of the film morphology

Atomic force microscopy (AFM): The elastomer films were placed between two poly(methyl methacrylate) plates and specimens were prepared by cutting ultra-thin sections cryogenically (−120 °C) with a Leica FCS microtome fitted with a histo cryo diamond knife (Diatome). AFM operating in tapping mode was carried out in air under ambient conditions with a Dimension 3100 connected to a NanoScope IV controller (Veeco Instruments, Santa Barbara, USA). The silicon cantilever comprised a nominal spring constant of 40 N/m and a resonance frequency of 360 kHz. Scanning electron microscopy (SEM): SEM images were taken with a JEOL JSM-5410 scanning microscope using a working voltage of 5 keV.

Transmission electron microscopy (TEM-EDX): The latex films were placed between two poly(methyl methacrylate) plates and specimens were prepared by cutting ultra-thin sections cryogenically (−120 °C) with a Leica FCS microtome fitted with a histo cryo diamond knife (Diatome). The sections were collected on nickel grids and stained with osmium tetroxide vapor for 2 h prior to examination. The cross-sections of the films were examined with a Philips CM 20 transmission electron microscope operating at 10 keV. EDXS spectra were taken with a Noran high purity Germanium EDX detector (TN-5500 Series II).

2.7. Characterization of the rubber network

An in-depth assessment of the rubber network microstructure was the topic of two previous publications [36,37], which we refer to for details. We have studied the given sample series with a focus on entanglement effects, and we here summarize the most relevant basic principles, as we discuss below some of the previously published results under a different viewpoint.

Equilibrium swelling measurements: To determine the crosslink density of the photo-vulcanized NR and IR latex films equilibrium measurements were carried out in accordance with the theory of Flory and Rehner [38,39]. From each solid film, 10 samples with a dimension of 2 × 2 cm were cut and weighed on an analytical balance with an accuracy of 0.1 mg. The samples were placed in vials and equilibrated with toluene (20 mL) for 48 h at 21 °C. The swollen films were removed from the solvent, blotted onto tissue paper and were weighed immediately. The films were then dried to constant weight under vacuum at 25 °C and re-weighed. The effective crosslink density (1/M) in mol/cm² was calculated and determined in agreement with recently published work and was averaged over 10 specimens [40].

Rubber multiple-quart (MQ) solid-state NMR spectroscopy: Proton NMR was used to determine the degree of crosslinking on a local (molecular) level based upon the quantitative measurement of the segmental residual (time-averaged) dipole–dipole coupling constant, \( d_{\text{res}} = d_{\text{res}}/2\pi \) in units of Hz [36,41,42]. As compared to isotropic liquids, this quantity is non-zero due to the restrictions on the network chain ends posed by crosslinks and also entanglements. It is related to the effective crosslink density via 1/M, as shown in Refs. [36,41,42]. The reference coupling \( d_{\text{ref}} \) is model dependent and has been determined to 617 Hz/kmol for NR [42] and IR [37], respectively. The method not only yields an average \( d_{\text{res}} \), but also its distribution function in case the network is inhomogeneously crosslinked. The \( d_{\text{res}} \) distribution was measured and analyzed according to previously published procedures [36,41,42], and characterized by its average (\( d_{\text{av}} \)) and width in terms of the standard deviation \( \sigma \). Finally, the method also provides the fraction of defects, i.e., isotropically mobile chains that do not carry load, such as loops and dangling chains.

Additional NMR experiments have been carried out on samples swollen in deuterated toluene to different degrees up to swelling equilibrium [36]. First, this leads to a higher and more realistic measure of the defect content, as long dangling chain may relax slowly on contribute to transient elasticity in the bulk, but are fully relaxed in the swollen state. Second, a back-extrapolation of \( D_{\text{av}} \) from differently swollen samples to its apparent value in the bulk provides a measure of the true (chemical) crosslink density of the network, referred to as phantom reference state (PRN), see Refs. [36,37]. The difference between this value and the \( D_{\text{av}} \) measured in bulk provides a measure of the entanglement contribution to the elasticity.

The measurements were performed with a Bruker minispec mq20 spectrometer operating at 0.5 T with 90° pulses of 1.7 μs length and a dead time of 12 μs. The experiments were carried out at 60 °C.

2.8. Characterization of the tensile properties

Tensile testing was performed with a ZWICK Z005 tensile tester in compliance with ASTM Standard D412-98a.

3. Results and discussion

The photo-vulcanization of diene-rubbers by thiol–ene addition reaction is characterized by short reaction times, low energy consumption and allows the manufacture of latex goods with good skin compatibility since any employment of skin hazardous process chemicals can be avoided [43]. These tremendous advantages
together with additional considerations such as ease of operation and operational safety concerns promoted the industrial implementation of the UV assisted pre-vulcanization for the commercial production of surgical gloves [44]. As the reliability of dipped latex articles is not only governed by the type of latex but also by the employed curing procedure it is crucial to assess the influence of the photo-vulcanization on network characteristics, film formation properties and corresponding tensile properties.

3.1. Determination of the crosslink kinetics

To evaluate the reactivity of the diene-rubber materials employed in the photo-vulcanization, the UV initiated addition of the thiol crosslinker to the C=CH double bonds was monitored by real time FT-IR spectroscopy. Fig. 2 depicts the consumption of the C=CH wagging band at 836 cm\(^{-1}\) versus the UV irradiation time. Upon 15 min of UV exposure and with 1.0 phr photoinitiator and thiol, respectively, IR films exhibit a significant depletion of the relative peak area up to 11\% whilst the decrease of the C=C double bonds in NR films amounts to 8\%. At higher concentrations of the process chemicals (5 wt.\%) a pronounced C=C consumption in the range of 28\% is observed in IR films. In contrast, the decrease of the C=C peak area is slightly lower in NR films (24\%). Account has to be taken into the fact that the infrared measurements of solid films may not fully reflect the reaction conditions in the liquid latex where other process parameters such as the polarity of the process chemicals or the diffusion of the process chemicals in the latex particles play a significant role [18]. However, the results give evidence that in IR films the depletion of C=C double bonds proceeds at a higher rate compared to NR. Since the UV assisted pre-vulcanization via the thiol-ene reaction is a free radical induced process the lower number of crosslinks observed in NR may be attributed to the presence of radical scavenging proteins. NR is derived from the Hevea brasiliensis tree and consists of a considerable amount of organic components including proteins (2–3 wt \%), fatty acids (1–1.5 wt \%) and lipids (1–1.5 wt.\%) [45–47]. Previous work has shown that not only lignin but also proteins can act as natural antioxidants [48,49]. Regarding NR latex, it was repeatedly demonstrated that the proteins present in the latex sap terminate free radical reactions such as the grafting of methacrylic monomers among them methyl methacrylate or 1,9-nonandioldimethacrylate [50–52]. In terms of thiol-ene crosslinking, these data clearly support the finding of the decreased reactivity of NR films compared to IR.

3.2. Determination of the network structure

Both crosslink density and spatial inhomogeneities of thiol-ene crosslinked diene-rubber films were determined by \(^1\)H multiple-quantum (MQ) solid-state NMR spectroscopy. It should be noted that a detailed NMR study of thiol-ene crosslinked NR and IR samples has already been published in two papers aimed at a fundamental microscopic understanding of the swelling process and the influence of entanglements [36,37]; selected data are here discussed in some more detail with regards to the materials’ characteristics. The normalized distribution widths of the residual dipolar—dipolar couplings which reflect the homogeneity of the crosslinked rubber matrix are depicted in Fig. 3a. The results clearly show that the crosslink distribution is strongly governed by the vulcanization procedure. In film state photo-vulcanization promotes highly homogeneous elastomer-networks which are comparable to sulfur cured systems (\(< \sigma/\sigma_{av} < 0.15\) whilst somewhat broader spatial crosslink distributions (0.15 < \(\sigma/\sigma_{av} < 0.3\) are obtained by the UV assisted pre-curing in latex state [42]. In contrast to thermally peroxide-cured NR samples (\(\sigma/\sigma_{av} > 0.3\)) photo-vulcanized networks do not exhibit higher crosslink densities as second component that can be attributed to radical chain scission reactions [42]. Due to the absence of any bimodal distribution of the crosslinks, the experimental data give an indication that UV pre-cured latex particles exhibit no core—shell structure with a highly crosslinked shell and a slightly crosslinked core [26].

In order to address topologically trapped entanglements, the samples were not only measured in dried state but also at different degrees of swelling using deuterated toluene as solvent. In Fig. 3b the apparent defect content in dried and swollen photo-vulcanized NR and IR samples is compared. A low defect fraction (\(< 5\%\)), comparable to hydperoxide-cured NR samples can be observed in dried state which is less dependent on either vulcanization procedure or type of latex [26,42]. The bulk measurements in dried state reflect quickly relaxing low molecular weight defects including short loops and dangling ends. With respect to peroxide-cured NR materials, the defect fraction is considerably higher (>20\%) related to chain scission reactions at higher temperatures [42].

However, when removing the entanglement constraints during swelling in toluene a completely different performance can be observed. Whilst low crosslinked samples comprise up to 90\% non-elastic chains, a distinctive decrease below 30\% is obtained with increasing crosslink density. This behavior gives an indication that the defect fraction is governed by long precursor chains which are highly entangled in the elastomer bulk and may comprise long relaxation times. Whilst the defect content in peroxide-cured NR samples does not increase upon swelling due to the contributions of short chain fragments, this trend is also observed in sulfur cured NR samples or poly(dimethylsiloxane) based elastomers [40,42,53].

The comparison of the NMR results to equilibrium swelling measurements is provided in Fig. 4. A very good linear correlation of the results from the two methods is observed, with deviations from a unity slope (dashed line) that are well within the uncertainties related to the different model assumptions. The entanglement-free phantom reference network (PRN) result obtained by back extrapolation of measurements on swollen samples correlates with the swelling result with zero offset, providing a convincing proof of principle. and allows for an estimation of the near-constant entanglement contribution in the bulk. It is interesting to note that NR samples exhibit higher crosslink densities than IR films at a given illumination dose which does not reflect the
3.3. Characterization of the film morphology

To address the influence of the photo-vulcanization on both film formation properties and morphology of solid latex films SEM, TEM and AFM measurements were conducted. In Fig. 5a–d the cross-section of NR as well as IR latex films pre-cured with an irradiation intensity of 0.9 W/cm² upon two illumination passes are compared. Although both samples comprise comparable crosslink densities of 0.085 (NR) and 0.076 (IR) mmol/cm³, respectively, a striking difference between the corresponding film morphologies is achieved. For the pre-vulcanized NR sample, a smooth and continuous cross-section without defects and particle contours is observed. The coherent film morphology suggests that an efficient interparticle diffusion has occurred during the coalescence step of the film formation. In contrast, SEM micrographs of photochemically pre-cured IR samples exhibit single and partly coalesced latex particles being very polydisperse in size (~1–10 μm) and predominately spherical in shape. The inhomogeneous film morphology of IR latex films reflected by the separated particles gives a good indication that the polymer diffusion across the particle interfaces has not occurred sufficiently during the last step of the film formation process.

Both IR and NR latex comprise negatively charged particles that are held apart by electrostatic forces. Whilst the IR latex particles are stabilized by adsorbed surfactants the NR latex particles are surrounded by negatively charged protein-phospholipid layers that prevent particle coalescence. In addition, ammonia is usually added to commercial NR latex to further improve the colloidal stability. During the dipping process the electrostatic forces are overcome upon neutralization with calcium cations initiating the film formation. A subsequent drying step at elevated temperature removes the residual water and leads to further particle coalescence and to polymer chain diffusion across the particle boundaries [54]. As evidenced by NMR experiments, UV pre-cured IR and NR samples exhibit homogenous crosslink distributions after film formation which gives an indication that both pre-cured latices do not comprise a core–shell structure. As both network structure and glass transition temperature are comparable, the difference between the film formation properties of NR and IR materials might be mainly attributed to the protein and phospholipid layers of NR latex that promote particle coalescence during film formation [19]. Literature data would suggest that the film formation properties of UV pre-cured IR latex are strongly affected by the overall crosslink yields which increase the internal viscosity and the hardness of the particles hindering their coalescence. Zosel and Lay have shown in their work that the film formation properties of synthetic latices such as poly(butyl methacrylate) (PBMA) are substantially influenced by their crosslink densities. They observed that highly crosslinked PBMA particles do not undergo particle coalescence giving rise to brittle latex films with poor mechanical properties whereas non crosslinked PBMA particles formed homogeneous and coherent films [35].

To confirm the effect of the crosslink density on the film formation properties of thiol-ene pre-vulcanized IR latex, the pre-vulcanization was carried out with a lower light intensity of 0.4 W/cm² upon two illumination passes corresponding to a crosslink density of 0.046 mmol/cm³. Fig. 6a and b depict the characteristic morphology of the IR film formed from lightly crosslinked latex particles. The SEM micrographs clearly reveal that slightly crosslinked IR latex particles form latex films with smooth and almost structureless morphologies. Singular particles with

![Image](https://example.com/image.png)

Fig. 3. (a) Spatial crosslink distributions and (b) apparent, non-elastic defect fractions of thiol-ene crosslinked NR and IR after film formation. A part of these data is replotted from Ref. [37].

![Image](https://example.com/image.png)

Fig. 4. Network chain densities obtained from NMR experiments versus the results of equilibrium swelling measurements. Data replotted from Ref. [37].
distinctive contours are notably absent indicating an improvement in the particle coalescence.

The morphology of UV pre-vulcanized IR latex films in dependence on the crosslink density was further characterized by TEM and AFM measurements. Fig. 7a and b provide bright field TEM micrographs of IR latex films pre-cured with 0.4 and 0.9 W/cm², respectively. In order to increase the material contrast, the specimens were stained with osmium tetroxide that reacts with the C=C double bonds of the poly(isoprene). With respect to highly crosslinked films (see Fig. 7b), the TEM images reveal spherically shaped latex particles with sharp contours. The TEM micrographs support the results of the SEM measurements and confirm that full coalescence of the latex particles was retarded resulting in an incoherent film formation. When it comes to slightly crosslinked IR films (see Fig. 7a), the contours of the individual particles have disappeared. In addition, bright domains are observed at the border of the latex shell. EDX spectra were taken from the bright domains as well as the latex particles illustrated in Fig. 8a and b. Besides the characteristic Os signals (1.9, 8.9 and 13 keV) attributed to the previous staining and the Ni signals (0.9, 7.5 and 8.2 keV) from the TEM grid, the EDX spectrum of the latex particles reveal the C Kα peak at 0.2 keV and the O Kα peak at 0.5 keV. In the rubber matrix, the photoinitiator as well as the cross-link agent levels are below the detection limit. Hence, sulfur or phosphor signals are not detected with EDX. Regarding the bright domains observed in the TEM images, Ca and Cl signals at 2.8 and 3.7 keV are observed. The results indicate that the process chemicals of the coagulant bath including calcium carbonate and calcium salts are incorporated in the bulk material during the film formation forced by the coagulation dipping process.

From the cross-sections of the IR films pre-cured with 0.4 and 0.9 W/cm², also AFM phase-contrast images were taken to characterize the viscoelastic properties. In these measurements obtained in tapping mode the dark contrast regions correspond to soft domains, whereas regions with light contrast correspond to hard domains. As illustrated in Fig. 9a and b, it is interesting to note that...
the boundaries of slightly crosslinked IR particles are partly disrupted suggesting that the particles have been fused together. In addition, similar to the TEM micrographs light domains with a sharp shape are observed at the boundaries of the partly fused latex particles. EDX spectra of these domains show a relatively high amount of Ca whereas no Cl signal can be detected. The results give a good indication that the light domains represent calcium carbonate particles from the coagulant bath.

With respect to highly crosslinked IR films (see Fig. 9c and d) the AFM images display sharp polyhedral contours and a regular packing. The majority of the observed particle boundaries are not disrupted confirming that the particle coalescence was hindered during the film formation process. The darker layer surrounding the particles may be attributed to surfactants such as sodium dodecyl sulfate that are widely used in the stabilization of the raw material. A similar morphology is observed in phase contrast images of NR,

![TEM micrographs](image)

**Fig. 7.** TEM micrographs (bright field) of dipped IR films photochemically pre-cured with an irradiation intensity of (a) 0.4 and (b) 0.9 W/cm².

![EDX spectra](image)

**Fig. 8.** EDX spectra of dipped IR films photochemically pre-cured with an irradiation intensity of (a) 0.4 and (b) 0.9 W/cm².
latex particles where the double layers of proteins and phospholipids are depicted as dark areas at the surface of the particles [46]. From the AFM measurements it can be further obtained, that the pre-cured rubber particles are inhomogeneously covered with dark streaked layers. In Fig. 10a and b the cross-section of highly cross-linked IR latex films are provided that has been imaged under “hard-tapping” and “soft-tapping” conditions. Imaging under different tapping forces leads to different extents of deformation in softer and more rigid regions that makes the characterization of liquids on both organic and inorganic surfaces feasible and represents an applicable tool to characterize material surfaces without adsorbed soft molecular layers [55]. It can be clearly shown that the dark structures observed under a small force vanish when imaging is performed with higher forces suggesting that the dark areas comprise liquid layers related to surfactants used in the stabilization of IR latex during storage.

Besides the illumination intensity or the concentration of the crosslink chemicals, the crosslink density of UV pre-cured latex particles is also governed by the distribution and diffusion of the photoinitiator and the thiol in the rubber particles [18]. In terms of sulfur pre-vulcanized NR latex particles, Ho and Khew have proposed that the diffusion rate of the process chemicals and the crosslink rate determine the distribution of the crosslinks in the rubber particles. Hence, a highly crosslinked shell together with a soft non crosslinked vulcanized core is achieved if the diffusion rate of the crosslink chemicals is considerably lower than the reaction rate of the crosslinking. Previous work of Che at al. has confirmed that peroxide-cured NR latex particles provide core–shell structures since the crosslinking reaction proceeds too fast to ensure a sufficient diffusion of the peroxide crosslinker inside the particle. In contrast, sulfur cured NR latex particles, using dipentamethylene-thiuram tetrasulfide as sulfur source, are characterized by narrow spatial crosslink distributions which Che at al. mainly relate to the slow crosslink kinetics [26].

In terms of photo-vulcanization, the diffusion of the photoinitiator and the thiol across the water phase into the latex particles occurs during the 2 h stirring of the reaction mixture at room temperature. Hence, the majority of the required crosslinking chemicals is already present in the latex particles during the photo-vulcanization which proceeds within minutes whereas thermal processes such as the accelerated sulfur vulcanization require reaction times in the range of hours [26]. As a consequence homogeneous networks are obtained although the reaction time of the thiol-ene photo-vulcanization is much faster than the diffusion rate of the chemicals. However, our previous work has demonstrated that the diffusion rate of the chemicals play a key role during the stirring time.

Fig. 9. Phase contrast images (tapping mode) of dipped IR films photochemically pre-cured with an irradiation intensity of (a,b) 0.4 and (c,d) 0.9 W/cm². Zone A and B highlight the sample areas which are magnified out of in Fig. 9b and d, respectively.
where a low polarity of the photoinitiator and the thiol crosslinker is eminent to obtain high crosslink yields and good mechanical properties of thiol-ene pre-cured NR films [18].

3.4. Determination of the mechanical properties

Fig. 11a provides the tensile properties of both NR and IR latex films pre-cured with a radiation intensity of 0.4 and 0.9 W/cm², respectively. With respect to pre-cured NR latex films the tensile strength rises with increasing exposure dose and amounts up to 30 ± 2 MPa. In terms of IR latex, no values could be obtained from films pre-cured with 0.9 W/cm² upon two and three illumination cycles since the incoherent film formation leads to brittle films with extensive macroscopic cracks. Although an improved film formation is obtained at lower exposure doses corresponding to crosslink densities <0.06 mmol/cm³, the tensile strength does not exceed 5 MPa. It has to be considered that compared to NR, IR comprises poor wet gel strength, low amount of branching, reduced gel content and low Mooney viscosity which can be associated with the different microstructure and stabilization of IR and results in considerably lower tensile properties of the uncured raw material [19,56].

To provide coherent IR films with higher crosslink densities the photo-vulcanization was carried out in solid state after the film formation. Fig. 11b illustrates the tensile strength of both NR and IR latex films versus the exposure dose employed in the UV illumination of the solid films. It can be clearly shown that both rubber materials provide comparable tensile properties in the range of 26 ± 2 MPa upon an exposure dose >2 J/cm². From the results it can be concluded that NR as well as IR latex films can be successfully crosslinked by the thiol-ene reaction and provide excellent mechanical properties when the photo-vulcanization is carried out in solid films. It should be noted that a detailed correlation of the macroscopic (obtained from the Mooney-Rivlin analysis of mechanical data) and the microscopic properties (characterized by DQ NMR) of thiol-ene cured elastomers is the subject of a separate publication [37].

4. Conclusions

In the present work thiol-ene chemistry has been employed to photo-vulcanize diene-rubbers, particularly NR and IR, in latex state as well as in solid film state. By following the crosslink kinetics of NR and its synthetic counterpart with real time infrared spectroscopy a higher crosslinking reactivity is determined for IR films that can be attributed to the absence of natural radical scavengers (e.g. proteins). After film formation the main characteristics of these elastomer-based thiol-ene networks have been determined.
and their influence on film formation properties, film morphology and corresponding tensile strength has been highlighted. 1H multiple-quantum (MQ) solid-state NMR experiments revealed that photo-vulcanization in film state promotes homogenous networks with narrow spatial crosslink distributions which somewhat get broader if the photo-vulcanization was carried out in latex state. In both cases the distributions did not show a second component which gives a strong indication that UV pre-cured latex particles do not comprise core–shell structures with highly crosslinked shells and lightly crosslinked cores. Additional NMR experiments of toluene-swollen samples further demonstrated that elastomer-based thiol-ene networks are characterized by a low amount of short chain defects (<5%). In terms of film formation, TEM, SEM and AFM measurements revealed that highly crosslinked IR latex particles suffer from inhomogeneous film morphologies with only partial coalescence of the latex particles. In contrast, NR films exhibit smooth and uniform film morphologies which are less dependent on the crosslink density of the latex particles. As the macroscopic properties such as the tensile strength are directly related to the film formation properties, UV pre-cured NR films comprise good tensile properties whilst highly crosslinked IR films are brittle and suffer from substantial cracking. However, in film state, photo-vulcanization leads to excellent tensile strengths (26 ± 2 MPa) of both NR and IR materials.

Acknowledgments

This study was performed at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the Comet K1 program and the “Produktion der Zukunft” program of the Austrian Federal Ministry for Transport, Innovation and Technology and of the Austrian Federal Ministry for Economy, Family and Youth with contributions of University of Leoben and Semperit Technische Produkte GmbH. PCCL is funded by the Austrian Government and the State Governments of Styria, Lower Austria and Upper Austria.

References
