

## Dual Crosslinking of Carboxylated Nitrile Butadiene Rubber Latex Employing the Thiol-ene Photoreaction

Dietmar Lenko,<sup>1</sup> Sandra Schlögl,<sup>1</sup> Armin Temel,<sup>1</sup> Raimund Schaller,<sup>2</sup>  
Armin Holzner,<sup>2</sup> Wolfgang Kern<sup>3</sup>

<sup>1</sup>Polymer Competence Center Leoben GmbH, Roseggerstraße 12, Leoben 8700, Austria

<sup>2</sup>Semperit Technische Produkte GmbH, Triester Bundesstraße 26, Wimpassing 2632, Austria

<sup>3</sup>Chair of Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, Leoben 8700, Austria

Correspondence to: S. Schlögl (E-mail: sandra.schloegl@pcccl.at)

**ABSTRACT:** At present, the most common used crosslinking process for carboxylated nitrile butadiene rubber (XNBR) latex is an accelerated sulfur curing system with zinc oxide. To avoid allergenic reactions related to residual accelerator levels in dipped XNBR latex articles such as medical gloves, a dual curing process has been developed combining thermal and photochemical crosslinking reactions. The two-step procedure involves the formation of covalent and ionic bonds to ensure good mechanical properties of the final products. The photochemical thiol-ene reaction is used to generate covalent crosslinks between the remaining C=C double bonds of the butadiene units whereas the carboxylic moieties are conventionally cured with divalent metal oxides (ZnO) under elevated temperature (formation of ionic crosslinks). The photochemical curing step is carried out both in the latex phase using a falling film photoreactor (pre vulcanization) as well as in the solid phase by UV irradiation of dried XNBR films (post vulcanization). The mechanical properties and crosslink densities of the cured XNBR films are determined and the influence of selected curing parameters is assessed. The results give evidence that a combined approach of thermal pre vulcanization and photochemical post vulcanization makes the production of latex articles (e.g., gloves) with tailored properties and good skin compatibility feasible. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2735–2743, 2013

**KEYWORDS:** elastomers; mechanical properties; crosslinking; photochemistry

Received 23 October 2012; accepted 28 December 2012; published online 1 February 2013

DOI: 10.1002/app.38983

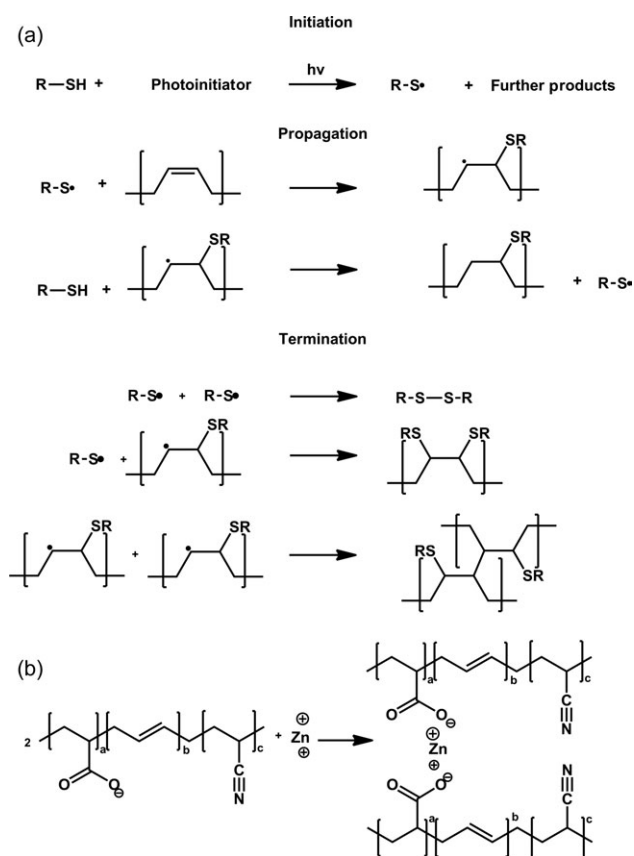
### INTRODUCTION

While natural rubber (NR) latex has been already known by the Aztecs since the 15th century, the production and application of synthetic rubber materials has not emerged until the beginning of the 20th century. The synthesis of carboxylic elastomers was first patented in 1930 and since then, the research on synthetic elastomer materials including co- and terpolymers such as carboxylated nitrile butadiene rubber (XNBR) has steadily increased.<sup>1</sup> Currently, the production of industrial quantities of XNBR latex involves radical emulsion polymerization techniques employing thermal initiators such as peroxides. Characteristic products made of hydrophilic XNBR latex include oil-resistant dipped goods, seals, and coatings. In addition, XNBR is often blended with other elastomer materials such as NR to enhance the performance of basic commodities based on rubber (e.g., tires).<sup>2–5</sup>

The physical and mechanical properties of XNBR latex articles are significantly influenced by the monomer composition of the

terpolymer as well as the employed crosslinking strategy. In particular, the glass transition temperature and the polarity of the uncured XNBR are rising with increasing acrylonitrile content whereas the flexibility at low temperature decreases.<sup>2</sup>

Furthermore, rubber materials are characterized by a long-range elasticity that is obtained after a crosslinking process, where the formation of a three-dimensional network transforms a plastic polymer into an elastomeric material. Through the remaining C=C double bonds of the butadiene units of the XNBR, covalent crosslinking sites are available making the thermal curing with either peroxides or sulfur in the presence of accelerators feasible. Moreover, the carboxylic groups represent versatile crosslink sites for the formation of both ionic and covalent bonds. In particular, the crosslink reactions involve the formation of amides and urea-bonds with polyamine salts and polyisocyanates, the formation of ester links with polyepoxides and polyols or the formation of anhydrides between two carboxylic groups at elevated temperature.<sup>6</sup> Besides covalent crosslinks, the



**Scheme 1.** Reaction mechanisms of the dual crosslinking of XNBR-latex using (a) the photochemical thiol-ene reaction and (b) the thermal crosslinking with ZnO.

mechanical properties of XNBR articles are mainly governed by ionic bonds that are formed between the carboxylic moieties in the presence of salts and oxides of multivalent metals (e.g., ZnO and MgO).<sup>7</sup>

The most common curing methods for XNBR in rubber industry include the sulfur vulcanization in the presence of ZnO and thermal crosslinking with peroxides combined with ZnO. With respect to the conventional sulfur curing system, XNBR latices with covalently bound accelerator groups are commercially available. These modified latices offer the advantage that the final cured latex articles comprise a low allergenic risk due to the absence of free residual accelerators (e.g., thiurams, mercaptobenzothiazoles, or dithiocarbamates). In addition to these established curing processes, previous studies have shown that XNBR can be covalently crosslinked by high energy radiation such as gamma-rays or e-beam.<sup>8–11</sup>

In the present work, we focus on a dual cure approach for the crosslinking of XNBR latex. On the one hand, covalent bonds are accomplished via the UV-assisted thiol-ene reaction and, on the other hand, the conventional thermal curing with ZnO is employed to generate ionic crosslinks (see Scheme 1). Our previous work has shown that the UV curing with the thiol-ene reaction represents a versatile and innovative procedure for the crosslinking of NR latex. It ensures short reaction times, ambi-

ent curing temperatures, and the substitution of noxious process chemicals that often elicit allergenic reactions of the human skin. As a consequence, UV crosslinked latex articles are characterized by good skin compatibilities and furthermore exhibit high tensile strengths.<sup>12–14</sup>

The photochemical addition of thiols to C=C double bonds represents a well-known reaction that is widely used for photo polymerization and photo crosslinking reactions. The thiol-ene reaction is initiated via the excitation of a selected photoinitiator upon UV illumination. Once formed, the free photoinitiator radicals react with thiol moieties under a hydrogen transfer leading to the formation of thiyl radicals. Following an anti-Markovnikov addition reaction, the thiyl radicals add to C=C double bonds under the formation of thioethers and carbon centered radicals. Various termination reactions include the formation of disulfides, thioethers, and covalent carbon-carbon bonds.<sup>15–17</sup>

In this work, we employed the thiol-ene reaction to accomplish covalent crosslinks between the butadiene units of the polymer chains of the XNBR latex. While the photochemical crosslinking of NR latex was predominately carried out in liquid phase using a falling film reactor,<sup>13</sup> we have studied both the photochemical pre vulcanization of XNBR latex in the liquid phase as well as the photochemical postvulcanization of XNBR carried out in the solid phase (UV postcuring and dual-curing). Due to the substantial differences between synthetic and natural latices involving chemical structure, reactivity, and film formation properties, different cure behavior and different mechanical properties of the final latex films are observed. A further objective of the present study is to evaluate crucial parameters of the dual crosslinking process in order to obtain XNBR latex films with enhanced mechanical and physical properties. The crosslink kinetics of the thiol-ene reaction is characterized by real-time Fourier transformation infrared (FT-IR) spectroscopy. The influence of the light intensity and the level of the photochemicals (photoinitiator and thiol crosslinker) on the consumption of the C=C double bonds is studied.

Moreover, the tensile properties (e.g., tensile strength, Young's modulus, elongation at break) and the crosslink densities of dual crosslinked XNBR latex films are determined in dependence on various process parameters (e.g., ZnO level, light intensity). The results give evidence that the two-step procedure is a promising way to produce XNBR latex articles (e.g., medical gloves) with tailored properties and low allergenic potential.

## EXPERIMENTAL

### Materials and Chemicals

XNBR latex (Nipol LX 556) with a dry rubber content of 45 wt % and a pH-value of 8.3 was purchased from a commercial supplier (ZEON, Japan). Ethyl 2,4,6-trimethylbenzoylphenylphosphinate (Lucirin TPO-L) was used as photoinitiator and was supplied by BASF (Ludwigshafen, Germany). The crosslinking agent trimethylolpropantris-3-mercaptopropionate (Tri-Thiol) was obtained from Bruno Bock Thiochemicals (Marschacht, Germany). Chloroform and all other chemicals were

obtained from Sigma-Aldrich (St. Louis, Missouri) and were used without further purification.

#### UV-Assisted Pre vulcanization of XNBR Latex

The first step of the UV-assisted pre vulcanization involved the emulsification of both the photoinitiator as well as the thiol crosslinker in deionized water. The emulsion was then added to the XNBR latex. The concentration of the photochemicals in the reaction mixture amounted to 1.0 phr (parts per hundred of rubber). After mixing the latex formulation for 2 h at room temperature with a magnetic stirrer, the UV pre vulcanization was carried out in a falling film photoreactor (tailor made) following the optimized procedure previously described for NR latex.<sup>13</sup> The latex formulation was illuminated with a UV immersion lamp (Hereaus; Hg medium pressure lamp emitting wavelengths in the range from 240 to 420 nm). The light intensity on the latex film surface was determined with a spectroradiometer (Solatell©, Solacope TM) and amounted to 0.9 and 1.1 J/cm<sup>2</sup>, respectively. The latex formulation was conveyed through the photoreactor at least three times and after each cycle a pre vulcanized liquid latex sample was collected.

#### Thermal Pre vulcanization with ZnO

Regarding the thermal pre vulcanization, a KOH solution (1 wt %) was added to the XNBR latex under stirring to raise the pH-value from 8.3 to 10.<sup>6,18,19</sup>

In the next step, a ZnO dispersion was admixed to the latex obtaining ZnO levels of 0.5, 1.0, and 2.0 phr. Each mixture was then stirred at elevated temperature (50°C) for 2 h by means of a magnetic stirrer.

#### Preparation of XNBR Latex Films

The XNBR latex films were prepared with a conventional coagulant dipping process. Prior to the dipping of the latex films, porcelain formers were cleaned with deionized water and acetone and then heated at 120°C for 10 min. The formers were dipped into a coagulant bath containing calcium salts (coagulant), calcium carbonate (release agent), and surfactants. After drying at 120°C, the formers were immersed in the precured XNBR latex for 20 s, and then withdrawn. Subsequently, the latex films were dried (120°C for 15 min), powdered with corn starch, and stripped from the formers. The film thickness accomplished with the selected dipping parameters ranged from 150 to 250 μm.

#### UV-Assisted Post vulcanization of XNBR Latex Films

Both thermally as well as photochemically precured XNBR latex films were post vulcanized employing the UV-assisted reaction pathway. In this case, an emulsion containing 0.5 phr photoinitiator and 0.5 phr thiol were added to the precured latices prior to the dipping step. After stirring the precured latex formulation for 2 h at room temperature, dipped XNBR films were prepared. The post vulcanization was carried out under air with a medium pressure Hg lamp (Hereaus) using a light intensity in the range from 0.3 to 1.2 J/cm<sup>2</sup>.

#### Real-Time FT-IR Measurements

To characterize the UV-assisted crosslinking, real-time FT-IR measurements were performed. The samples were prepared by spin casting a solution of 2.0 wt % XNBR in chloroform con-

taining the photoinitiator and the thiol onto gold-coated glass substrates. The concentration of the photochemicals is described in the "Results and Discussion" section. The samples were placed on a specimen holder in a large angle reflectance IR cell (Harrick Scientific) and the cell was flooded with inert gas (nitrogen) to avoid photo-oxidation upon UV irradiation. The UV illumination was carried out with a UV spot curing unit (Efos Novacure) using wavelengths between 290 and 410 nm. The thiol-ene reaction was monitored during UV illumination with a light intensity of 1.1 W/cm<sup>2</sup>. The IR spectra were taken with an FT-IR spectrometer (Spectrum One, Perkin Elmer) after defined irradiation times and the absorbance peak areas were calculated using Spectrum 3.02 and Spectrum Time Base 1.1 software.

#### Equilibrium Swelling Measurements

Swelling measurements according to the Flory-Rehner method<sup>20,21</sup> were carried out to determine the crosslink density ( $\nu$ ) and the molar mass between the crosslinks ( $M_c$ ) of the cured XNBR films. Small samples of the dried XNBR latex films were cut (2 × 2 cm), weighed and placed in glass vials which were filled with chloroform. The vials were stored at 21°C for 48 h and after this period it was assumed, that the equilibrium swelling time was reached.<sup>22–24</sup> The samples were taken out of the solvent, placed in air for 30 s to ensure that the solvent was evaporated from the surface and were weighed again. The network density and the molar mass were calculated using eq. (1), where  $V_p$  is the volume fraction of the polymer in the swollen state,  $V_s$  the molar volume of the solvent, and  $\chi$  the Flory-Huggins interaction parameter. The Flory-Huggins interaction parameter was calculated with the following equation,  $\chi = 0.487 + 0.228 \times V_p$  in accordance to literature.<sup>25</sup>

The density of the XNBR latex films ( $\rho_{\text{polymer}}$ ) was determined by the hydrostatic weighing method using a Sartorius balance with a resolution of ±0.1 mg. The apparent weight of the precured XNBR films was measured in air and *n*-heptane and the density was calculated as follows,  $\rho_{\text{polymer}} = (G_{\text{air}} \times \rho_{n\text{-heptane}} - G_{n\text{-heptane}} \times \rho_{\text{air}}) / (G_{\text{air}} - G_{n\text{-heptane}})$  where  $\rho_{n\text{-heptane}}$  and  $\rho_{\text{air}}$  are the densities of air and *n*-heptane at 20°C.  $G_{\text{air}}$  corresponds to the weight determined in atmosphere and  $G_{n\text{-heptane}}$  is the weight determined in *n*-heptane. Ten samples were measured and the resulting mean value of the density of crosslinked XNBR films was  $\rho_{\text{XNBR}} = 1.013 \text{ g/cm}^3$ . The density and the Flory-Huggins interaction parameter were used to calculate the network density according to eq. (1).

$$\nu = \frac{-\ln(1 - V_p) + V_p + \chi^* V_p^2}{V_s^* \left( V_p^{\frac{1}{3}} - \frac{V_p}{2} \right)} \quad (1)$$

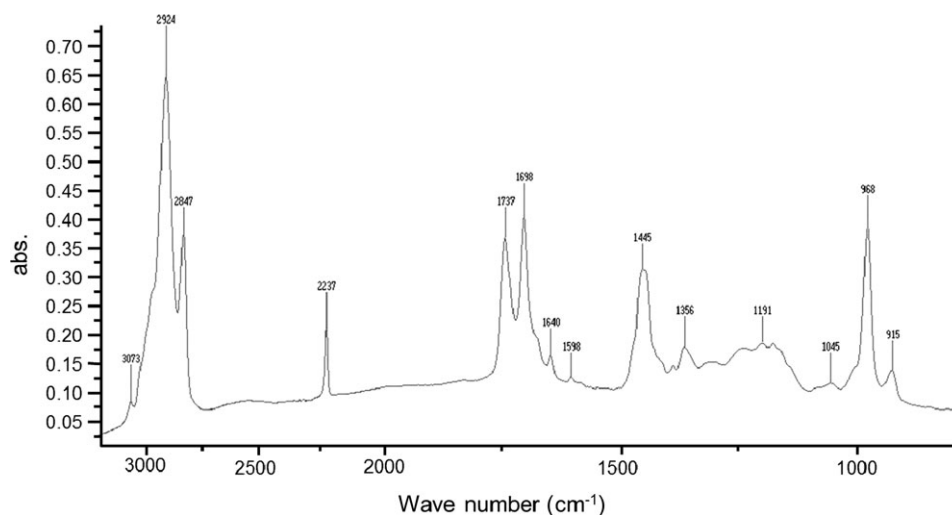
#### Tensile Testing

The mechanical properties of crosslinked XNBR latex films including Young's modulus, tensile strength, and ultimate elongation were determined with a Zwick tensile tester Z010 in compliance with European standard.<sup>26</sup>

## RESULTS AND DISCUSSION

#### Determination of the Photochemical Crosslink Kinetics

The UV-induced curing behavior of XNBR latex via the thiol-ene reaction was monitored with real-time FT-IR spectroscopy.



**Figure 1.** FT-IR spectrum of a XNBR latex film containing 5.0 wt % photochemicals.

In Figure 1, the FT-IR spectrum of a XNBR sample containing 5.0 wt % photoinitiator and 5.0 wt % thiol is depicted. In Table I, the characteristic IR absorption bands of XNBR are assigned according to literature data and listed in descending order.<sup>27</sup> Since the decrease of the thiol-bands and the appearance of thioether signals, which arise when forming the thiol-ene networks in XNBR films, cannot be detected quantitatively (both moieties show weak absorption signals in their infrared spectra), the decrease of the C=C double bonds was monitored during UV exposure.

Figure 2 illustrates the consumption of the C=C double bonds of the main chain (968 cm<sup>-1</sup>) in dependence on the irradiation time. The results clearly show that the control sample containing neither photoinitiator nor thiol does not show a significant decrease (1%) of the C=C band. With 5.0 phr photoinitiator added the decrease of the relative peak area amounts to 8% attributed to the formation of short chain carbon-carbon crosslinks. However, the maximum depletion of the peak area (12%) is observed in the presence both of photoinitiator and thiol. Previous Raman studies of UV crosslinked NR samples have revealed that thioether links are formed predominately in the presence of photoinitiator and thiol while the formation of short chain carbon-carbon crosslinks is negligible.<sup>13</sup>

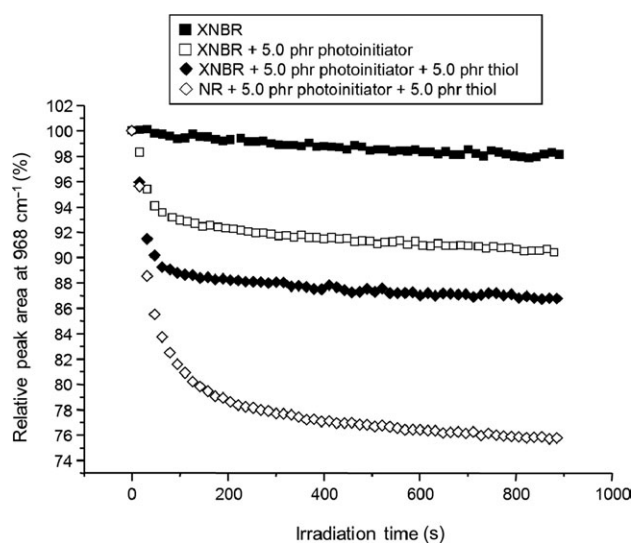
Comparing the infrared results of XNBR latex to photochemically cured NR samples that have been crosslinked by using the

**Table I.** Characteristic Infrared Bands Observed in Cured XNBR Films

Wave number (cm <sup>-1</sup> )	Assignment
2924	CH <sub>2</sub> stretching (butadiene)
2847	CH <sub>2</sub> stretching (acrylonitrile)
2237	CN stretching
1737	C=O stretching
1445	CH deformation
968	H-C=C deformation (main chain)
915	H-C=C deformation (side chain)

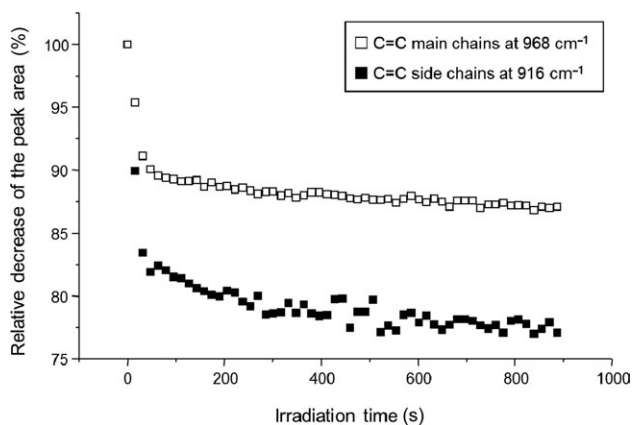
same amount of photoinitiator and thiol, a lower reactivity of the main chain C=C double bonds is observed.<sup>13</sup> The NR samples show a relative decrease of the C=C band up to 24% whereas in XNBR samples the C=C double bond band consumption does not exceed 12%. The higher reactivity of the polyisoprene units in natural rubber latex can be attributed to the higher electron density of the double bond due to the presence of the methyl group. As reported in literature, the crosslink kinetics of thiol-ene reactions are governed by the electron density of the C=C double bonds. Hoyle et al.<sup>17</sup> have shown that the reactivity of the ene component increases with increasing electron density of the carbon-carbon double bond.

Account has to be taken into the fact that XNBR comprises not only main chain C=C double bonds (1,4 addition) but also a small amount (≈18–20%) of side chain vinyl bonds (1,2 addition).<sup>28,29</sup> In Figure 3, the relative peak areas of the main chain and side chain vinyl bonds versus the UV irradiation time are



**Figure 2.** Monitoring the depletion of the C=C main chain double bonds (infrared signal at 968 cm<sup>-1</sup>).





**Figure 3.** Monitoring the depletion of C=C side chain double bonds (916 cm<sup>-1</sup>) and C=C main chain double bonds (968 cm<sup>-1</sup>) in XNBR films containing 5.0 wt % photoinitiator and 5.0 wt % thiol using FT-IR spectroscopy.

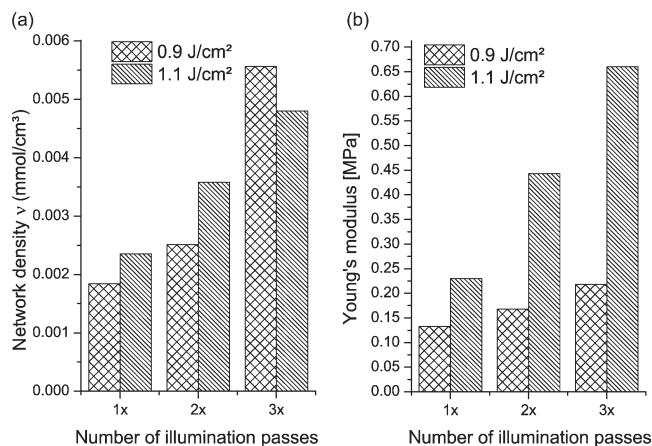
compared. The results give evidence that the vinyl bonds of the side chains exhibit a higher reactivity than the C=C double bonds of the main chain at a given level of photochemicals (5 wt %). With respect to the thiol-ene reaction, the higher reactivity of vinyl groups located at terminal positions is well known and is attributed to the higher mobility of the vinyl side chains.<sup>17,30</sup>

### Photochemical Crosslinking

In order to determine the network characteristics and the mechanical properties of photochemically cured XNBR films, the UV-assisted pre vulcanization of XNBR latex was carried out in a falling film photoreactor. The design of the falling film reactor ensures both a continuous and homogenous UV illumination of the liquid reaction formulation in thin films. The precuring was carried out with 1.0 phr thiol and 1.0 phr photoinitiator, respectively, while the light intensity of the immersion lamp amounted to 0.9 and 1.1 J/cm<sup>2</sup>.

Various methods can be used to determine the network density of elastomeric networks including the measurement of the shear modulus and NMR measurements.<sup>31,32</sup> To obtain the crosslink density of photochemically crosslinked XNBR films, equilibrium swelling experiments in compliance with the Flory-Rehner method were performed.<sup>20</sup> The method is based on the theory that there is a balance in the swollen state, where the elastomer is a gel-like elastic solution. As swelling is driven by the solvation of the polymer chains, a force balance which is given in the swollen equilibrium state leads to eq. (1).<sup>21</sup> This equation is only applicable in the equilibrium state, where the restoring force, which appears due to the stretching of the elastomeric network, is equal to the solvation force.<sup>20</sup>

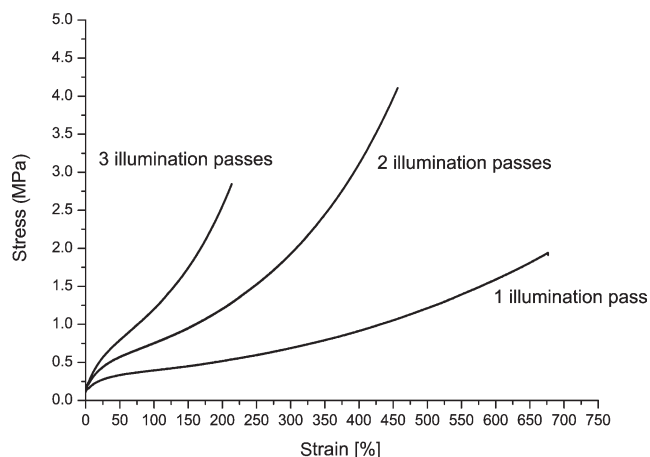
In Figure 4(a), the crosslink densities of XNBR films precured with 0.9 and 1.1 J/cm<sup>2</sup> are shown in dependence on the number of illumination passes carried out in the falling film reactor. When it comes to photochemical crosslink reactions, the intensity of the incident light controls the rate of initiation. According to Lambert-Beer's law, the number of initiating radicals increases proportionally with the incident light intensity.<sup>33</sup> The



**Figure 4.** (a) Network density and (b) Young's modulus of XNBR films precured with 0.9 and 1.1 J/cm<sup>2</sup> versus the number of illumination passes carried out in the falling film reactor.

results of the swelling measurements of UV cured XNBR latex films reveal that an increase of the light intensity leads to higher crosslink densities, which has also been observed in the UV-assisted crosslinking of NR latex.<sup>12</sup> Moreover, at a given light intensity, the crosslink density rises after each pass in the falling film reactor. In particular, by using a light intensity of 0.9 J/cm<sup>2</sup> the crosslink density increases from 0.0018 mmol/cm<sup>3</sup> after the first pass to 0.0056 mmol/cm<sup>3</sup> after the third illumination pass. From these results, it can be concluded that covalent crosslinks are formed due to the photochemical pre vulcanization via thiol-ene reaction. It should be noted that these results are comparable to the swelling properties of conventional sulfur pre vulcanized XNBR films that comprise crosslink densities ranging from 0.0019 to 0.0030 mmol/cm<sup>3</sup> in dependence on the sulfur and accelerator concentration.

Besides the network structure, the tensile properties of UV precured XNBR films were determined. Figure 4(b) illustrates the Young's modulus of photochemically precured XNBR films versus the number of illumination passes and Figure 5 provides



**Figure 5.** Stress-strain curves of XNBR latex films photochemically precured with a light intensity of 0.9 J/cm<sup>2</sup> in dependence on the number of illumination passes carried out in the falling film photoreactor.

**Table II.** Mechanical Properties (Young's Modulus, Elongation at Break, and Tensile Strength) of UV Precured XNBR Films (1.0 phr photochemicals)

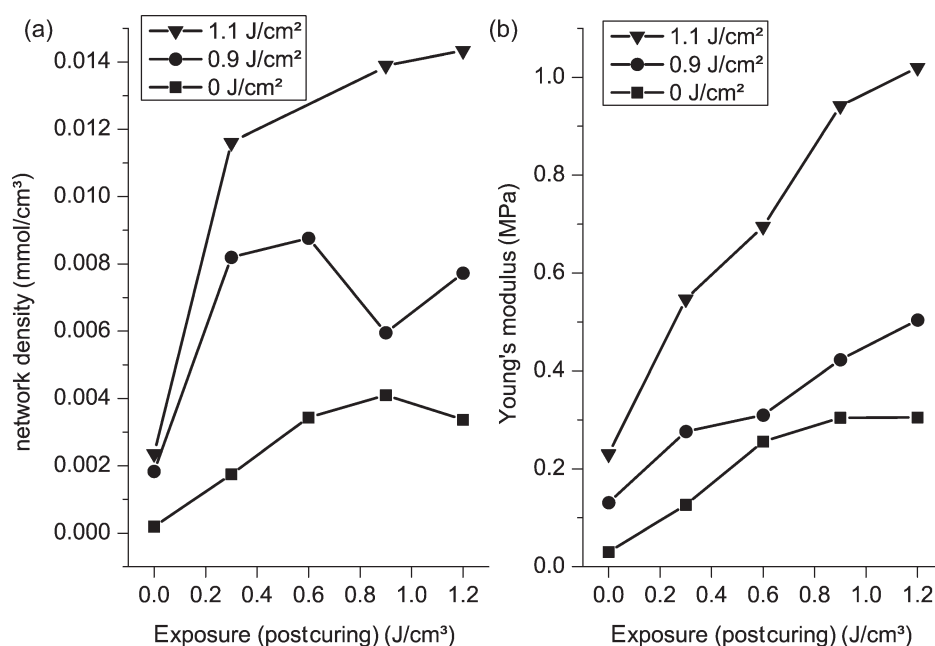
Light intensity ( $\text{J}/\text{cm}^2$ )	Number of illumination passes	Network density ( $\text{mmol}/\text{cm}^3$ )	Young's modulus (MPa)	Stress at break (MPa)	Strain at break (%)
0.9	1	0.0018	0.13	2.71	905
	2	0.0025	0.17	2.25	690
	3	0.0056	0.22	2.35	630
1.1	1	0.0024	0.23	2.57	645
	2	0.0036	0.44	2.96	490
	3	0.0048	0.66	2.21	300

stress–strain curves of XNBR films precured with  $0.9 \text{ J}/\text{cm}^2$  after various illumination steps. From the curves it can be observed that the Young's modulus is increasing after each illumination pass carried out in the falling film reactor while the ultimate elongation at break decreases. As shown in Figure 4(b), the same trend is obtained with higher crosslinked XNBR films employing a light intensity of  $1.1 \text{ J}/\text{cm}^2$  in the precuring step. These results provide a good correlation with the number of covalent crosslinks determined via the equilibrium swelling measurements [shown in Figure 4(a)]. However, in terms of tensile strength, the results clearly show that the increasing crosslink density and modulus do not correspond to improved tensile properties. As shown in Figure 5 and Table II, the tensile strength of UV precured XNBR films does not exceed 4 MPa.

To increase the number of covalent crosslinks and to enhance the tensile properties, we combined the UV-assisted precuring of the liquid state with a photochemical postcuring of the solid films. In Figure 6, the crosslink density and Young's modulus of UV precured films ( $0.9$  and  $1.1 \text{ J}/\text{cm}^2$ ) are illustrated versus the UV exposure used in the postcuring step. It can be observed

that the Young's modulus increases significantly upon UV illumination of the solid precured XNBR films. The maximum increase of the Young's modulus ranges from  $0.3$  to  $0.8 \text{ MPa}$ . With respect to the equilibrium swelling measurements of UV pre- and post-cured XNBR films, the results reveal that the network density of XNBR films, precured with  $1.1 \text{ J}/\text{cm}^2$ , increases steadily with an increasing exposure dose used in the postcuring step. However, XNBR samples photochemically precured with  $0.9 \text{ J}/\text{cm}^2$  exhibit a maximum crosslink density at  $0.55 \text{ J}/\text{cm}^2$  UV exposure (postvulcanization step).

In Table III the results of the tensile tests are summarized. While the network density, the Young's modulus, and the ultimate elongation at break correlate with the UV exposure dose used in the postcuring step, the tensile strength cannot be increased significantly. From these results, it can be concluded that the UV-induced postvulcanization leads to an additional formation of covalent crosslinks. However, taking the low tensile strengths into account, the results suggest that the covalent bonds formed via the thiol-ene reaction are not sufficient to ensure high tensile strengths. It has to be considered that this



**Figure 6.** Young's modulus and network density in dependence on the exposure dose of the UV-assisted pre- and postcuring step (the lines are only a guide for the eye). The values given in the insert refer to the prevulcanization intensity.

**Table III.** Mechanical Properties (Elongation at Break and Tensile Strength) of UV Precured and UV Postcured XNBR Films

Light intensity precuring (J/cm <sup>2</sup> )	0		0.9		1.1	
	Stress at break (MPa)	Strain at break (%)	Stress at break (MPa)	Strain at break (%)	Stress at break (MPa)	Strain at break (%)
0	2.6	1200	2.7	905	2.5	645
0.3	3.0	760	3.2	570	3.3	445
0.6	2.2	460	4.5	650	3.6	420
0.9	3.1	525	4.3	555	3.9	385
1.2	3.4	550	4.0	505	2.9	335

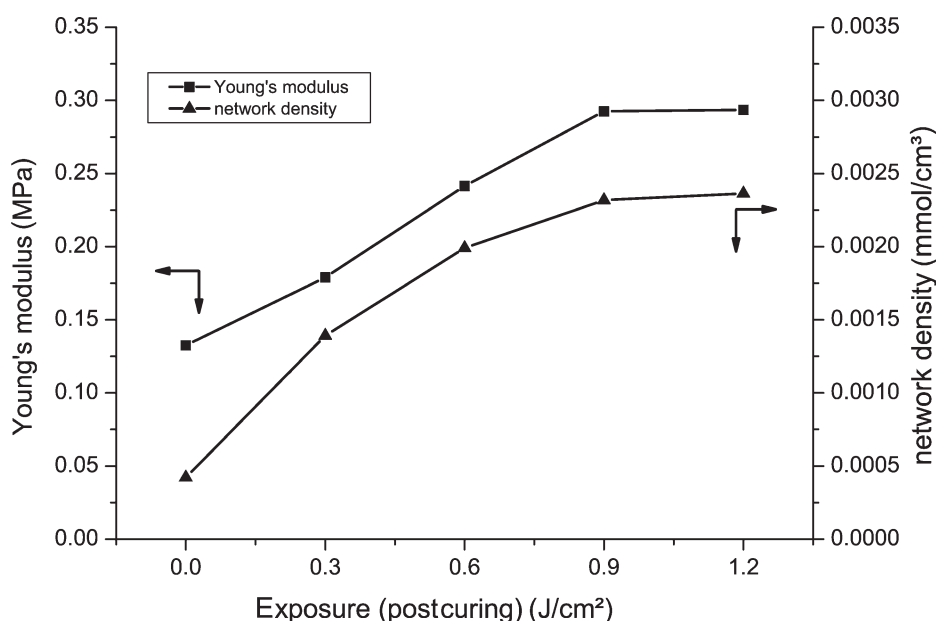
effect is also observed in conventionally cured XNBR systems. Previous work has shown that sulfur and peroxide cured XNBR films suffer from low tensile strengths in the absence of multivalent salts such as ZnO that form ionic crosslinks. Tobolsky and Eisenberg<sup>34,35</sup> postulated that the high tensile properties of ionic crosslinked carboxylic rubbers are attributed to ionic aggregation and cluster formation that lead to a two-phase, reinforced rubber network. According to Cooper et al.,<sup>36</sup> local stresses are reduced within the rubber network due to an interchange of ionic crosslinks under mechanical stress leading to enhanced tensile properties. Another mechanism is proposed by Halpin<sup>37</sup> suggesting that a wide-meshed network is crucial for high tensile strengths. Although the correlation between the ionic nature of rubber crosslinks and high tensile properties remains undisclosed, the consequences for the mechanical properties are well described. Carboxylic rubbers vulcanized by metal oxides are characterized by a considerable reinforcement including enhanced tensile strength and modulus. However, without covalent crosslinks the ionic rubber network suffers from poor compression set, low elongation at break and reduced tensile strength at higher temperature. Consequently, several authors

have proposed that both covalent as well as ionic crosslinks are required to obtain good mechanical properties and ageing stabilities.<sup>6,34,36,38–47</sup>

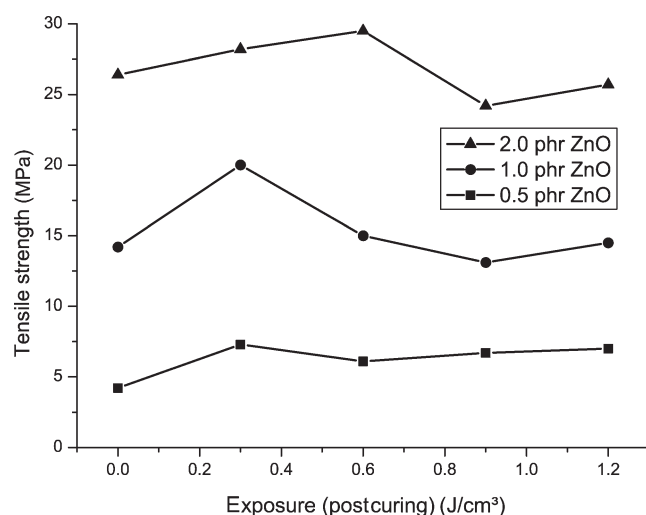
### Dual Crosslinking

Since the tensile strength plays a key role in the application of dipped latex goods (e.g., gloves), a dual crosslinking approach was developed aiming at the formation of covalent and ionic crosslinks. To enhance the tensile strength of UV cured XNBR latex films, we combined a thermally induced precuring using ZnO with a UV-assisted postcuring of the solid films. The thermal precuring was carried out with various amounts of ZnO (0.5, 1.0, and 2.0 phr), whereas a given photochemical concentration of 0.5 phr was used in the photochemical postcuring step.

In Figure 7, the network density and Young's modulus of dual crosslinked (pre-vulcanization with 0.5 phr ZnO) XNBR films are provided in dependence on the UV exposure employed in the postvulcanization step. It is evident that a substantial increase of the crosslink density of thermally precured XNBR films is achieved with the photochemical postcuring step due to



**Figure 7.** Young's modulus and crosslink density of thermally precured (0.5 phr ZnO) XNBR latex films in dependence on the UV exposure used in the UV-assisted postcuring (the lines are only a guide for the eye).



**Figure 8.** Tensile strength of dual crosslinked XNBR latex films containing different levels of ZnO versus the UV exposure in the postcuring (the lines are only a guide for the eye).

the UV-induced formation of covalent crosslinks. With respect to the thermal precuring, account has to be taken into the fact that the Flory-Rehner equation is less sensitive to ionic crosslinks. Different models have to be applied for the calculation of network densities when the network contains pH-sensitive moieties.<sup>22,48</sup> Consequently, the ionic network structure of the precured samples cannot be determined reliably by the Flory-Rehner method.

With respect to the tensile properties, a substantial increase of the tensile strength and Young's modulus is observed that is attributed to the reinforcement by the formation of ionic crosslinks. In Figure 8, the tensile strength versus the UV exposure (postvulcanization) and the ZnO concentrations (prevulcanization) are depicted. It can be observed that the concentration of ZnO strongly influences the tensile properties of the XNBR films. By rising the level of ZnO from 0.5 to 2.0 phr, an enhancement of the tensile strength from  $4 \pm 2$  MPa to  $26 \pm 2$  MPa can be obtained. Due to the photochemical postcuring step, an additional increase of the tensile strength is accomplished. In particular, the tensile strength of XNBR films thermally precured with 2.0 phr ZnO can be improved from  $26 \pm 2$  MPa to  $30 \pm 2$  MPa. It is interesting to note that the tensile strength of thermally precured XNBR films reaches an optimum between 0.2 and 0.4 J/cm<sup>2</sup> while higher illumination doses (>0.4 J/cm<sup>2</sup>) lead to a decrease again.

Due to its resistance against nonpolar solvents, XNBR is often used for the manufacture of dipped medical articles such as gloves. From the results it can be concluded that the tensile properties of dual crosslinked XNBR films meet the quality requirements of the European Standard EN 455-2 for medical and surgical gloves.<sup>26</sup> Since conventional vulcanization agents are substituted by photochemicals, latex allergies related to accelerator residues can be avoided. Consequently, the dual crosslinking of XNBR represents a new way toward the production of low allergenic medical gloves.

## CONCLUSIONS

The present study clearly shows that polar rubber materials such as XNBR can be crosslinked successfully with the thiol-ene reaction. It is demonstrated that the UV-assisted formation of covalent crosslinks can be carried out both in liquid (UV pre-vulcanization of the latex) as well as in the solid state (UV post-vulcanization of solid films). The FT-IR investigations on the crosslink kinetics reveal that XNBR exhibits a lower reactivity than NR while the vinyl groups of the side chain comprise a higher reactivity than the vinyl groups of the polymer backbone.

The formation of the covalent bonds is further confirmed by the results of the equilibrium swelling measurements and the measurements of the Young's modulus. It can be shown that both network density and Young's modulus are increasing with rising light intensity giving evidence to the formation of a tighter network. Since the tensile strength of carboxylic containing rubber materials is mainly governed by the presence of ionic crosslinks a dual crosslink approach has been developed. Due to a thermal precuring with ZnO followed by a photochemical crosslinking, both ionic and covalent crosslinks are generated leading to a substantial increase of the tensile strength. The results confirm that the two-step process makes the production of XNBR films feasible that display good mechanical properties and a low allergenic potential.

## ACKNOWLEDGMENTS

The research work of this paper was performed at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Transport, Innovation and Technology and Federal Ministry for Economy, Family and Youth with contributions by the Chair of Chemistry of Polymeric Materials (University of Leoben, Austria) and the Semperit Technische Produkte GmbH (Wimpassing, Austria). The PCCL is funded by the Austrian Government and the State Governments of Styria and Upper Austria.

## REFERENCES

1. I.G. Farbenindustrie. France. FR 701102. July 19, 1930.
2. Röthemeyer, F.; Sommer, F. *Kautschuk-Technologie*; Hanser: München, 2006; Vol.2.
3. Dunn, J. R.; Vara, R. G. *Rubber Chem. Technol.* **1983**, *56*, 557.
4. Hashimoto, K.; Maeda, A.; Hosoya, K.; Todani, Y. *Rubber Chem. Technol.* **1998**, *71*, 449.
5. Pal, K.; Das, T.; Pal, S. K.; Das, C. K. *Polym. Eng. Sci.* **2008**, *48*, 2410.
6. Brown, H. P. *Rubber Chem. Technol.* **1963**, *36*, 931.
7. Brown, H. P. US Pat.2,626,248, 1953.
8. Peixinho, C.; Tavares-Ratado, P.; Tomás, M.; Taborda-Barata, L.; Tomaz, C. *Br. J. Dermatol.* **2008**, *159*, 132.
9. Yagami, A.; Suzuki, K.; Saito, H.; Matsunaga, K. *Allergol. Int.* **2009**, *58*, 347.



10. Meade, B.; Weissman, D. N.; Beezhold, D. H. *Int. Immunopharmacol.* **2002**, *2*, 225.
11. Ownby, D. R. *J. Allergy Clin. Immunol.* **2002**, *110*, S27.
12. Schlögl, S.; Temel, A.; Schaller, R.; Holzner, A.; Kern, W. *J. Appl. Polym. Sci.* **2012**, *124*, 3478.
13. Schlögl, S.; Temel, A.; Schaller, R.; Holzner, A.; Kern, W. *Rubber Chem. Technol.* **2010**, *83*, 133.
14. Schlögl, S.; Temel, A.; Kern, W.; Schaller, R.; Holzner, A. *Kautsch. Gummi Kunstst.* **2010**, *63*, 187.
15. Hoyle, C. E.; Bowman, C. N. *Angew. Chem. Int. Ed.* **2010**, *49*, 1540.
16. Hoyle, C. E.; Bowman, C. N. *Angew. Chem.* **2010**, *122*, 1584.
17. Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 5301.
18. Kells, A.; Groves, R. *Latex 2006*, **2006**, Paper 16.
19. Robertson, J.; Maloney, D.; Ghafoor, M. *Latex 2001*, **2001**, 61.
20. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, **1953**.
21. Flory, P. J.; Rehner, J. *J. Chem. Phys.* **1943**, *11*, 521.
22. Elliot, J.; Macdonald, M.; Nie, J.; Bowman, C. N. *Polymer* **2004**, *45*, 1503.
23. Chronska, K.; Przepiórkowska, A. *J. Appl. Polym. Sci.* **2009**, *114*, 1984.
24. Ain, Z. N.; Azura, A. R. *J. Appl. Polym. Sci.* **2011**, *119*, 2815.
25. Zaborski, M.; Kosmalska, A.; Gulinski, J. *Kautsch. Gummi Kunstst.* **2005**, *58*, 354.
26. EN 455-2:2009+A1:2011. *Medical Gloves for Single Use—Part 2: Requirements and Testing for Physical Properties*, **2009**.
27. Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley & Sons: Chichester, New York, Brisbane, Toronto, **1994**; Vol.2.
28. Van der Velden, G.; Didden, C.; Veermans, T.; Beulen, J. *Macromolecules* **1987**, *20*, 1252.
29. Hampton, R. R. *Anal. Chem.* **1949**, *21*, 923.
30. Lowe, A. B. *Polym. Chem.* **2010**, *1*, 17.
31. ISO 1827:2011. *Rubber, Vulcanized or Thermoplastic—Determination of Shear Modulus and Adhesion to Rigid Plates—Quadruple-Shear Methods*, 4th ed., 83.060 **2011**.
32. Illisch, S.; Menge, H.; Radusch, H.-J. *Kautsch. Gummi Kunstst.* **2000**, *53*, 206.
33. Crivello, J. V.; Dietliker, K.; Bradley, G. *Photoinitiators for Free Radical Cationic & Anionic Photopolymerisation*; J. Wiley in association with SITA Technology: Chichester, West Sussex, England, New York, **1998**; Vol.2.
34. Tobolsky, A. V.; Lyons, P. E.; Hata, N. *Macromolecules* **1968**, *1*, 515.
35. Eisenberg, A. *Macromolecules* **1970**, *3*, 147.
36. Cooper, W. J. *Polym. Sci.* **1958**, *28*, 628.
37. Halpin, J. C.; Bueche, F. *J. Polym. Sci. Part A: Gen. Pap.* **1965**, *3*, 3935.
38. Cooper, W. J. *Polym. Sci.* **1958**, *28*, 195.
39. Bhowmick, A. K.; De, S. K. *Rubber Chem. Technol.* **1980**, *53*, 107.
40. Rajeev, R. S.; De, S. K. *Rubber Chem. Technol.* **2002**, *75*, 475.
41. Ibarra, L.; Rodríguez, A.; Mora-Barrantes, I. *Polym. Int.* **2009**, *58*, 218.
42. Ibarra, L.; Rodríguez, A.; Mora, I. *Eur. Polym. J.* **2007**, *43*, 753.
43. Ibarra, L.; Marcos-Fernández, A.; Alzorriz, M. *Polymer* **2002**, *43*, 1649.
44. Ibarra, L.; Alzorriz, M. *J. Appl. Polym. Sci.* **2002**, *84*, 605.
45. Ibarra, L.; Alzorriz, M. *Polym. Int.* **2000**, *49*, 115.
46. Grossman, R. F. (Synthetic Products Company). USA. US Pat.4,952,634. August 12, **1988**.
47. Dolgoplosk, B. A.; Reikh, V. N.; Tinyakova, E. I.; Kalas, A. E.; Koryushenko, Z. A.; Sladkevich, E. G. *Rubber Chem. Technol.* **1959**, *32*, 328.
48. Brannon-Peppas, L.; Peppas, N. A. *Chem. Eng. Sci.* **1991**, *46*, 715.