

# Characteristics of the Photochemical Pre vulcanization in a Falling Film Photoreactor

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**ABSTRACT:** The photochemical pre vulcanization of natural rubber (NR) latex via the thiol-ene reaction is a new approach aiming at the replacement of noxious processing agents used in conventional sulfur vulcanization processes (e.g., accelerators) together with cost saving options. The crosslinking reaction involves the excitation of a selected photoinitiator with ultraviolet (UV) light which is followed by the formation of thioether links due to the thiol-ene addition reaction. The photochemical process is carried out in a falling film photoreactor which provides not only a continuous pre vulcanization process but also exhibits a technology which is already commercially well established. The main advantage of the falling film process lies in the short pre vulcanization time and the mild reaction temperature. Following the idea of the manufacture of low-allergenic surgical gloves made from NR latex without

compromising on the glove quality by means of physical performance, crucial process parameters of the falling film process have been determined and characterized in this study. Surgical gloves were made from the photocured NR latex which was pre vulcanized using selected process conditions. The physical properties including tensile strength, elongation, modulus, and crosslink density were examined together with the aging stability and the stability against high-energy radiation (sterilization with gamma rays). It was found that the UV light intensity, the number of illumination cycles, the choice of photoinitiator, and the thiol crosslinker play an important part in the glove quality. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3478–3486, 2012

**Key words:** crosslinking; elastomers; falling film photoreactor; photochemistry; surgical gloves

## INTRODUCTION

Ultraviolet (UV) light has been found to be widely applicable in modifying the properties of polymer bulk materials and polymer surfaces.<sup>1,2</sup> In the medical field, the numerous applications of radiation in polymer chemistry are ranging from UV crosslinked acrylates for dental materials to surface functionalized catheters with improved tissue compatibility.<sup>3,4</sup> In this work, UV light is used to crosslink liquid natural rubber (NR) latex via the thiol-ene reaction focusing on the manufacture of low-allergenic and accelerator-free surgical gloves.

At present, the most common crosslinking technique for NR latex in industrial use is the accelerated sulfur vulcanization, credited to Charles Goodyear and patented in the mid-19th century. Although the sulfur curing systems offer many advantages including the lack of oxygen and moisture sensitivity, they suffer from a serious drawback.<sup>5</sup> The accelerators which are used to lower the reaction temperature and to shorten the reaction

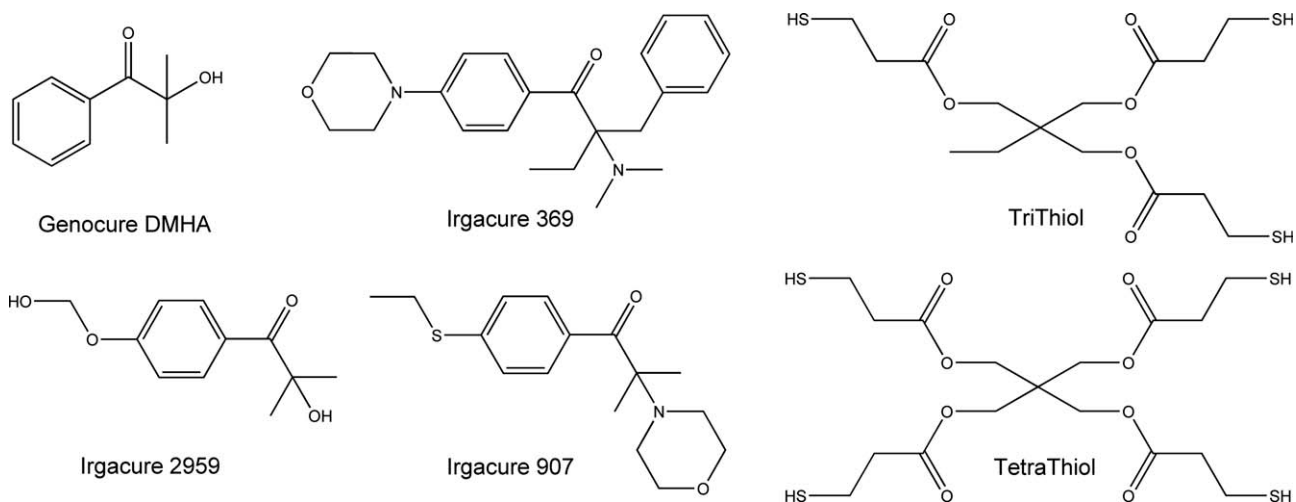
time pose a considerable risk of provoking allergic reactions.<sup>6–8</sup> Further potential human health hazards associated with dithiocarbamate-type and 2-mercaptobenzothiazole-type accelerators include a high risk of cytotoxicity and tissue irritancies, whereas their potential of carcinogenicity or genotoxicity is not yet fully clarified.<sup>9,10</sup>

To avoid the health concerns arising from accelerator residues in medical and surgical gloves, alternative crosslinking processes have been developed including curing with peroxides or crosslinking with high-energy radiation (e.g., e-beam and  $\gamma$ -rays).<sup>11,12</sup> In recent publications, new ways have been established to synthesize UV curable latex formulations on a laboratory scale.<sup>13</sup> However, it has to be considered that using these crosslinking techniques, new problems related to poor physical properties of the final products, high investment, and production costs or the usage of other noxious processing agents (e.g., acrylic monomers) can emerge.

The UV pre vulcanization of NR latex via the thiol-ene reaction, which has been described recently, offers a new approach to manufacture accelerator-free surgical gloves exhibiting a good biocompatibility together with a low amount of leachable compounds.<sup>14,15</sup>

Highly versatile thiol-ene chemistry can be used to prepare crosslinked polymers and is already used

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**Scheme 1** Chemical structures of the processing chemicals (photoinitiators/thiols) used in the photochemical crosslinking of NR latex.

in medical devices such as dental restoratives or drug release hydrogels.<sup>16,17</sup> The UV-induced reaction involves a radical addition of thiols to nonactivated C=C double bonds. Using thiol derivatives bearing more than two thiol moieties crosslinking of diene rubbers can be achieved efficiently.<sup>18,19</sup> To obtain a continuous UV irradiation of the NR latex, a falling film photoreactor is used. Falling film reactors are well known and are used in various industrial technologies including water waste treatment and preparative organic chemistry.<sup>20–22</sup> Due to the low-light transmissivity of NR latex, the concept of the falling film process allows a homogenous irradiation of the reaction mixtures in thin films with thicknesses in the range of millimeters. Compared with thin film reactors, there is no contact between the reaction medium and the UV lamp. As a consequence, the radiation intensity does not deplete during the various process cycles due to accumulated degradation products on the lamp surface. For the crosslinking of latex, this new technology, which operates at room temperature and is accomplished within minutes, allows enormous cost saving options compared with conventional sulfur vulcanization processes which are carried out at elevated temperatures for hours in batch processes.<sup>5</sup> Solid films are then prepared using a conventional coagulant dipping process.

The aim of this study was to find a correlation between crucial process and recipe parameters and the property profile of the final articles. This knowledge is important in the assessment of the new technology for industrial exploitation and makes the production of tailored latex articles feasible. The studies revealed that using optimized process parameters, the physical properties of UV prevulcanized surgical gloves clearly exceed the quality requirements of EN 455-2 (2000) and ASTM D 3577.

The excellent tensile strengths are paralleled with good aging and sterilization stabilities. The optimized tensile properties of UV prevulcanized NR latex goods together with the low-energy costs offer exciting prospects for future applications.

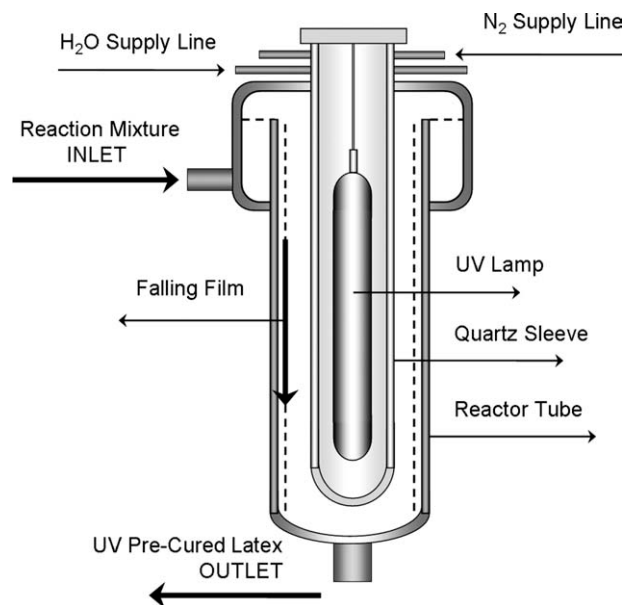
## EXPERIMENTAL

### Materials and chemicals

Natural concentrated rubber latex (high ammonia, 60 wt % dry rubber content) was obtained from a Malaysian supplier (Tapah, Malaysia). The photoinitiators 4-(2-hydroxyethoxy) phenyl-(2-propyl) ketone (Irgacure 2959) and 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (Irgacure 907) were purchased from CIBA Specialities (Basel, Switzerland). 2-Benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl) phenyl]-1-butanone (Irgacure 369) was supplied by Sigma-Aldrich (St. Louis, United States). The crosslinking agents trimethylolpropane tris(3-mercaptopropionate) (TriThiol) and pentaerythritol tetra(3-mercaptopropionate) (TetraThiol) were obtained from Bruno Bock Thiochemicals (Marschacht, Germany). The chemical structures of the photoinitiators as well as the thiol crosslinker are provided in Scheme 1. All other reagents were from Sigma Aldrich and were used without further purification.

### UV prevulcanization of NR latex

The schematic diagram of the pilot plant is provided in Figure 1. The falling film reactor was tailor made and comprised a coaxially positioned immersion lamp and a reservoir at the top. The immersion lamp was a medium pressure Hg UV-arc lamp with a maximum electrical power of 3.5 kW. To enhance the longevity of the UV system, the lamp was



**Figure 1** Schematic representation of a falling film photo-reactor used for the UV pre-curing of NR latex.

equipped with a quartz sleeve to provide water cooling for the absorption of the infrared radiation and was flooded with nitrogen. An eccentric screw pump conveyed the latex emulsion continuously from the storage tank to the reservoir atop the cylindrical falling tube of the reactor. The construction of the falling film reactor permitted the formation of a stable and continuous falling film with thicknesses below 1 mm. The falling film was cascading down the inner side of the reactor tube while undergoing UV irradiation. The outlet of the reactor tube was connected to a collecting vessel where the precured latex was collected after each illumination cycle.

The pre-vulcanization process was carried out by emulsifying the processing chemicals (photoinitiator and thiol crosslinker) in deionized water. The emulsion of the chemicals was then added to high-ammonia NR latex comprising a dry rubber content of 40 wt %. In this latex formulation, the concentration of both the photoinitiator and the thiol amounted to 1.0 phr (parts per hundred of rubber). The reaction mixture was stirred using a magnetic agitator in the storage tank at room temperature for 2 h.

The rheological measurements of the latex emulsion were performed on an Anton Paar MCR-301 rheometer comprising a parallel plate geometry (50 mm diameter) with a gap between the two plates of 0.05 mm. The shear rate was varied between 5 and 1000  $\text{s}^{-1}$ , and the temperature of the latex formulation was held at 20°C. Figure 2 illustrates the viscosity of the latex formulation containing 40 wt % dry rubber content versus the shear rate. In addition, the density of the reaction mixture was determined with a 1 mL pycnometer and amounted to 0.971 g/mL.

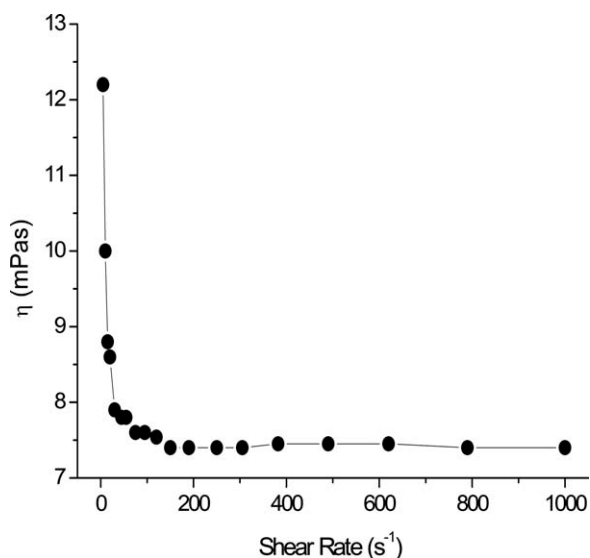
The pre-vulcanization in the falling film reactor was carried out with a lamp power ranging from 2.5 to 3.5 kW corresponding to an irradiation intensity from 0.7 to 1.1  $\text{W}/\text{cm}^2$  on the reactor surface. The light intensity into the falling film plane was determined with a spectroradiometer (Solatell, Solascope 2000<sup>TM</sup>). No light filter was used, and the wavelength range was between 240 and 460 nm. Due to the UV irradiation, the temperature of the latex mixture increased from room temperature (approx. 20°C) to a maximum of 38°C.

After irradiation, 0.3–1.0 phr of a high-molecular weight phenolic antioxidant was added to the precured latex, and the formulation was stirred by means of a magnetic agitator for 2 h at room temperature.

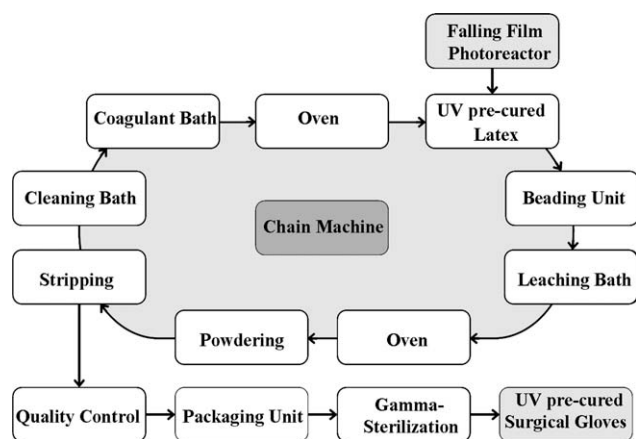
### Preparation of UV pre-vulcanized surgical gloves

For the manufacture of the surgical gloves, a coagulant dipping process was used on a semi-industrial scale. The gloves were produced on a continuous chain machine comprising a highly automatic production line where porcelain hand formers connected to a chain went through different process stations. The various production steps from the pre-vulcanized latex to the final product, the sterile surgical glove, are shown in Figure 3.

In the first step, the porcelain formers were cleaned with acidic and alkaline solutions to ensure an even and continuous deposition of the latex in the subsequent process steps. The porcelain formers were then rinsed with hot water and dried in an oven. The formers were then immersed in a coagulant bath containing calcium salts as coagulant. After the formers had been coated and dried, they were



**Figure 2** Viscosity of a NR latex formulation containing 40 wt % dry rubber content as a function of shear rate.



**Figure 3** Processing steps of the manufacture of UV pre-cured surgical gloves.

dipped in the precured latex, left for an appropriate dwell time and then were slowly withdrawn. The coagulant dipping gave a latex film with film thicknesses ranging from 200 to 300  $\mu\text{m}$ . The dipped wet latex film was allowed to build up sufficient wet-gel strength before the beading and leaching process were carried out. The beading step involved the rolling down of the topmost portion of the glove.

In the next process step, the leaching step, the gloves were immersed in hot water to reduce the protein levels and to lower the content of chemical residues. The gloves were finally dried in an oven which was followed by a powdering step using a powder slurry containing corn starch. The dried and powdered gloves were stripped from the formers, packaged, and sterilized with gamma rays using a  $^{60}\text{Co}$  source with an irradiation dose of 25 kGy.

### Tensile tests

The tensile tests were performed with a ZWICK Z010 tensile tester in compliance with ASTM Standard D412-98a.

### Determination of the crosslink density by equilibrium swelling studies

Early research by Flory and Rehner laid the foundations for the analysis of the equilibrium swelling which is commonly used to determine crosslink densities of polymer networks.<sup>23,24</sup> The equilibrium swelling measurements were carried out by cutting samples with dimensions of approximately 2 cm  $\times$  2 cm from the UV pre-cured surgical gloves. The samples were weighed on an analytical balance and placed in vials containing 20 mL of toluene. The rubber films were equilibrated in an oven for 48 h at 21°C. The swollen films were then taken out of the solvent, blotted onto filter paper to remove excess solvent on the sample surface, and weighed. The sam-

ples were dried to constant weight under vacuum at 25°C and reweighed. To calculate the crosslink density of the pre-cured sample, eq. (1) was used according to the Flory–Rehner Theory, where  $\nu$  stands for the effective crosslink density in  $\text{mol}/\text{cm}^3$  and  $\Phi_p$  for the volume fraction of the polymer in the swollen sample.  $\chi$  corresponds to the polymer–solvent interaction parameter of the Flory–Huggins theory and  $V_L$  is the molar volume of the solvent.

$$\nu = \frac{-\left(\ln(1 - \Phi_p) + \Phi_p + \chi \cdot \Phi_p^2\right)}{V_L \cdot \left(\Phi_p^{\frac{1}{3}} - \frac{\Phi_p}{2}\right)} \quad (1)$$

## RESULTS AND DISCUSSION

This work is aimed at the study of the relationship between crucial process parameters of the photochemical pre-curing in a falling film photoreactor and the resulting physical properties of the final articles. Although products for very different applications can be made from UV cured NR latex, the process optimization has been focused on the quality requirements of surgical gloves with respect to physical and mechanical properties.

### Effect of photoinitiator

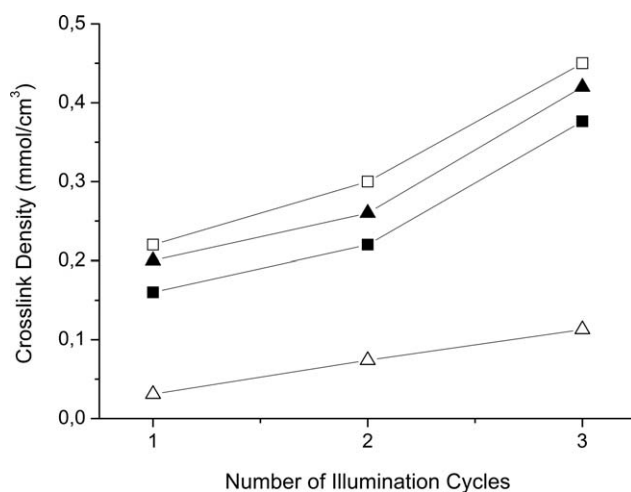
The initiation mechanism of the UV-assisted crosslinking of NR latex via the thiol-ene reaction involves the excitation and cleavage of a photoinitiator. In the pre-curing process, Type I photofragmenting photoinitiators, which undergo homolytic bond cleavage under UV irradiation to yield free radicals, have been used. In particular, the choice of unimolecular photoinitiators was based on their considerable advantages including high reactivity, thermal stability, and the absence of any additional coinitiators which are paramount when working with Type II photoinitiators.<sup>25</sup> Regarding the efficiency of the photoinitiator system, not only the reactivity of the compound but also the fit of the light source to the absorption spectrum of the photoinitiator, the transmission properties of the reaction mixture and photophysical data (e.g., quantum yield) have to be considered. The physical characteristics of the photoinitiators used in this study are compared in Table I.<sup>25–28</sup> However, when it comes to the crosslinking of hydrophilic rubber particles in a water-borne system account has to be taken into the fact that the curing efficiency may also depend on the diffusion and distribution of the processing chemicals in the polymer phase.

The first experiments in the pilot plant were carried out under air with a radiation intensity of 0.9

**TABLE I**  
**UV Absorption Characteristics (Molar Extinction Coefficient and Quantum Yields of the  $\alpha$ -Cleavage) of Commercial Photoinitiators Used in the UV Pre vulcanization of NR Latex**

Photoinitiator	$\epsilon_{222 \text{ nm}}$ (L/mol cm)	$\epsilon_{313 \text{ nm}}$ (L/mol cm)	$\Phi_{\alpha}$
Genocure DMHA	2800	90	0.2–0.3
Irgacure 2959	9400	490	0.38
Irgacure 907	5600	16,000	0.88
Irgacure 369	11,000	17,000	0.3

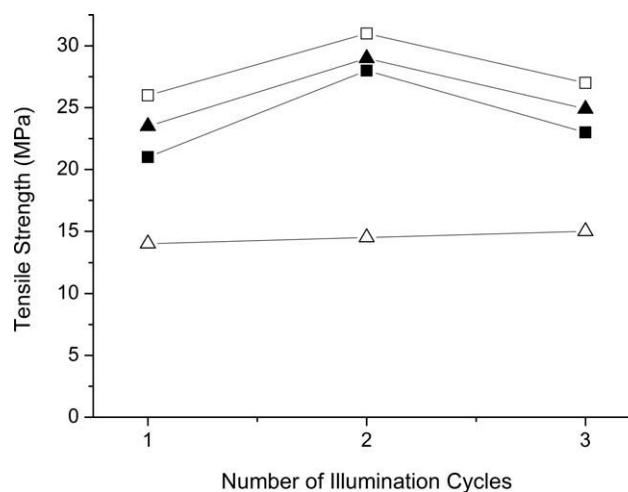
W/cm<sup>2</sup> and a TriThiol concentration of 1.0 phr. Figure 4 illustrates the crosslink density of nonsterile gloves precured with different photoinitiators (1.0 phr) versus the number of illumination cycles conducted in the falling film photoreactor. Besides the tensile tests, swelling measurements were used to confirm the formation of three-dimensional polymer networks due to the photochemical prevulcanization. The results clearly show that the choice of photoinitiator considerably influences the crosslink kinetics. Genocure DMHA and Irgacure 2959 are  $\alpha$ -hydroxyalkylphenone derivatives with similar quantum yields and comparable absorption characteristics (Table I).<sup>26,27</sup> Recent work on the UV curing of water-based urethane-acrylate coatings also revealed that both photoinitiators exhibit similar crosslink kinetics.<sup>28</sup> However, with respect to the photocuring of NR latex, the initiation with Genocure DMHA results in crosslink densities ranging from 0.13 to 0.38 mmol/cm<sup>3</sup> in dependence on the number of illumination passes, whereas the crosslink density does not exceed 0.1 mmol/cm<sup>3</sup> when using Irgacure 2959 as photoinitiator. These results suggest that the polarity of the photoinitiator represents a key parameter regarding the crosslink yields of the rubber



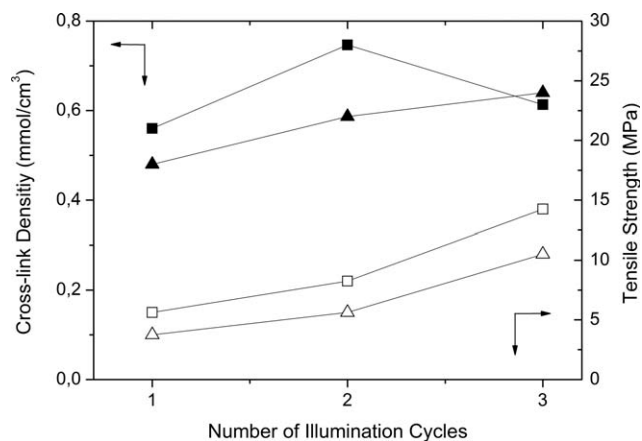
**Figure 4** Effect of the photoinitiator on the crosslink density in mmol/cm<sup>3</sup> of nonsterile surgical gloves with a given TriThiol level of 1.0 phr.

particles accomplished via the thiol-ene reaction. In contrast to Genocure DMHA, it has to be considered that Irgacure 2959 is a relatively polar photoinitiator which is used for applications in polar or water-based formulations.<sup>25,29</sup> The low-crosslink densities give an indication that the hydrophilic Irgacure 2959 may not efficiently diffuse in the hydrophobic latex particles in the mixing stage resulting in a low concentration of initiating radicals in the rubber particles during the UV process. This is endorsed by the results of the tensile tests provided in Figure 5. It can be shown that the tensile strength of nonsterile gloves precured with Irgacure 2959 lies between 12 and 14 MPa independent of the number of illumination cycles in the photoreactor. Regarding the prevulcanization with Genocure DMHA, an optimum of the tensile strength ( $28 \pm 3$  MPa) is obtained after the second illumination pass corresponding to a crosslink density of 0.24 mmol/cm<sup>3</sup>. It should be further noted that higher crosslink densities ( $>0.40$  mmol/cm<sup>3</sup>) achieved after three illumination cycles result in a decrease of the tensile properties ( $25 \pm 3$  MPa).

Although  $\alpha$ -hydroxyalkylphenone derivatives generate more radicals in very short UV-C (100–280 nm) and longer UV-B (280–315 nm) radiation,  $\alpha$ -aminoalkylphenone derivatives such as Irgacure 369 or Irgacure 907 exhibit absorption bands in the long wavelength range tailing to 400 nm. The long wavelength absorption (350–400 nm) reduces light scattering and allows a deeper light penetration. As a function of the wavelength ( $\lambda$ ), the scattered light intensity is proportional to  $\lambda^{-4}$ , resulting in a strong wavelength dependence which makes short wavelength light scatter more than long wavelength light.<sup>1,25</sup> Consequently, a more uniform through crosslinking of the rubber particles in the reaction



**Figure 5** Effect of the photoinitiator on the tensile strength in MPa of nonsterile surgical gloves with a given TriThiol level of 1.0 phr.



**Figure 6** Effect of the crosslink agent (1.0 phr) on the tensile strengths (in MPa) and crosslink densities (in mmol/cm<sup>3</sup>) of nonsterile gloves with a given Genocure DMHA content of 1.0 phr.

medium is expected. Compared with Genocure DMHA, it was found that the employment of  $\alpha$ -hydroxy-alkylphenones results in higher crosslink densities ranging from 0.18 to 0.45 mmol/cm<sup>3</sup>. In addition, an enhancement of the tensile strength from  $28 \pm 3$  to  $30 \pm 3$  MPa is observed. It is evident that the absorption characteristic and the reactivity of the photoinitiator influence the mechanical properties of the latex products, but it has to be considered that other properties of the photoinitiator such as yellowing can be important when assessing a technology for industrial exploitation. It is well known that photoinitiators with aromatic amine moieties such as Irgacure 369 or Irgacure 907 can produce colored cleavage products on exposure to UV light.<sup>25,30</sup> Thus, it should be noted that the prevulcanization with either Irgacure 369 or Irgacure 907 leads to bright yellow latex articles. To avoid colored byproducts, Genocure DMHA was used for the further crosslinking experiments.

### Effect of thiol crosslinker

Well known thiol-ene reactions involve the reaction of unsaturated C=C bonds with thiol derivatives such as alkyl thiols, thiol glycolate esters, or thiol propionate esters. From previous publications, it can be obtained that thiols based on propionate esters and glycolate esters comprise a higher reactivity compared with alkyl thiols due to a weakening of the thiol moiety by hydrogen bonding of the thiol hydrogen groups with the ester carbonyl.<sup>18,31</sup> Due to their commercial availability and widespread use, trimethylolpropane tris(3-mercaptopropionate) (TriThiol) and pentaerythritol tetra(3-mercaptopropionate) (TetraThiol) were used as crosslink agents in the photochemical prevulcanization.

The UV process was carried out with 1.0 phr of thiol and a given Genocure DMHA concentration of 1.0 phr, respectively. Figure 6 illustrates the tensile properties and crosslink densities of the gloves plotted against the number of illumination cycles conducted with a radiation intensity of 0.9 W/cm<sup>2</sup>. It could be shown that using TetraThiol as crosslink agent, lower crosslink densities (0.10–0.29 mmol/cm<sup>3</sup>) are obtained in comparison to the prevulcanization with the TriThiol that gives crosslink densities ranging from 0.15 to 0.38 mmol/cm<sup>3</sup>. These results give an indication that the differences in the crosslink densities may be largely attributed to the reactivity of the thiol derivatives. Recent research addressing the photopolymerization kinetics of acrylic monomers with TriThiol and TetraThiol has revealed that the trifunctional derivative leads to a higher conversion of the vinyl groups and exhibits higher polymerization rates.<sup>32</sup>

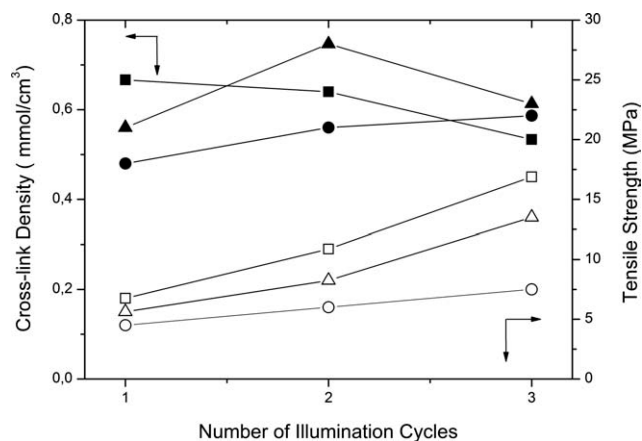
With respect to the tensile properties, it was found that the tensile strength of gloves cured with TetraThiol display a continuous increase over three illumination passes, up to 24 MPa, whereas the prevulcanization with TriThiol leads to an optimum of the tensile properties ( $28 \pm 3$  MPa) after the second illumination cycle in the falling film reactor.

### Effect of radiation intensity

For photochemical crosslinking to proceed efficiently, the absorption bands of the photoinitiator must overlap with the emission spectrum of the light source. Regarding the prevulcanization of the latex, an undoped medium pressure mercury lamp was used. The spectral energy distribution of the immersion lamp at different electrical powers is summarized in Table II. Besides the photoinitiator concentration, the incident light intensity controls the rate of initiation in photochemical crosslink reactions. When UV illuminating thick films, the number of light-induced radicals can be estimated by eq. (2) derived from Beer–Lambert's law. As shown in eq. (2), the number of initiating radicals ( $n$ ) increases proportionately with the incident light intensity ( $I_0$ ) and the quantum yield of the photoinitiator ( $\phi_i$ ) and

**TABLE II**  
Spectral Energy Distribution of the Immersion Lamp Obtained at 2.5 kW, 3.0 kW and 3.5 kW of Electrical Power

$\lambda$ (nm)	$\Phi$ at 2500 W lamp power (mW/cm <sup>2</sup> )	$\Phi$ at 3000 W lamp power (mW/cm <sup>2</sup> )	$\Phi$ at 3500 W lamp power (mW/cm <sup>2</sup> )
230–280	25	30	36
280–315	63	77	90
315–400	274	333	393
400–470	385	470	554



**Figure 7** Physical properties of nonsterile gloves with 1.0 phr Genocure DMHA and 1.0 phr TriThiol added as a function of the number of illumination cycles conducted in the pilot plant using various irradiation energies.

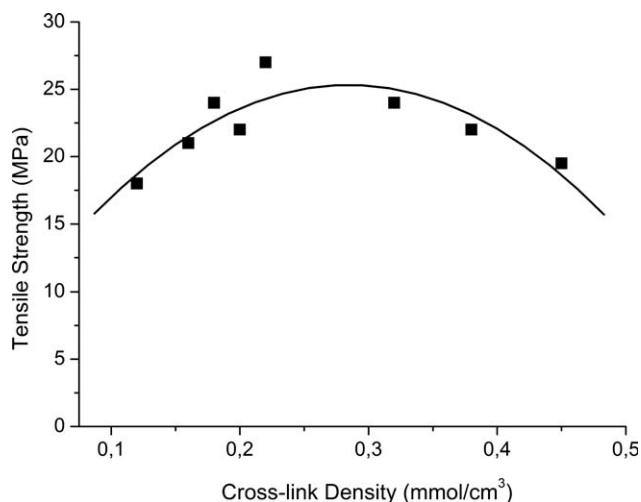
is also a function of the photoinitiator concentration ( $c$ ), the optical pathway ( $d$ ), and the extinction coefficient ( $\epsilon_\lambda$ ).<sup>25,33</sup>

$$n = I_0(1 - 10^{-\epsilon(\lambda) \cdot c \cdot d})\phi_i \quad (2)$$

The experiments to study the effect of radiation intensity on the mechanical properties of the latex gloves were carried out using 1.0 phr Genocure DMHA and 1.0 phr TriThiol, respectively. The values of crosslink densities and corresponding tensile strengths versus the number of illumination passes are provided in Figure 7. It can be clearly shown that an increase of the light intensity is paralleled by an enhancement of the crosslink density. From these results, it can be concluded that more photoinitiator radicals are generated at higher radiation intensities yielding a tighter rubber network. However, when correlating the crosslink densities obtained at various light intensities (0.7, 0.9, and 1.1 W/cm<sup>2</sup>) with the corresponding tensile properties (Fig. 8), it is evident that the tensile strength does not proportionately increase with the number of crosslinks. The results give evidence that higher crosslink densities (>0.30 mmol/cm<sup>3</sup>) result in a depletion of the physical properties. The lower physical properties of highly crosslinked latex particles may be explained by the film formation properties during the dipping process. Ho and Khew<sup>34</sup> have shown in their work that there is a balance between crosslink densities, film forming properties, and resulting mechanical properties.

#### Effect of oxygen

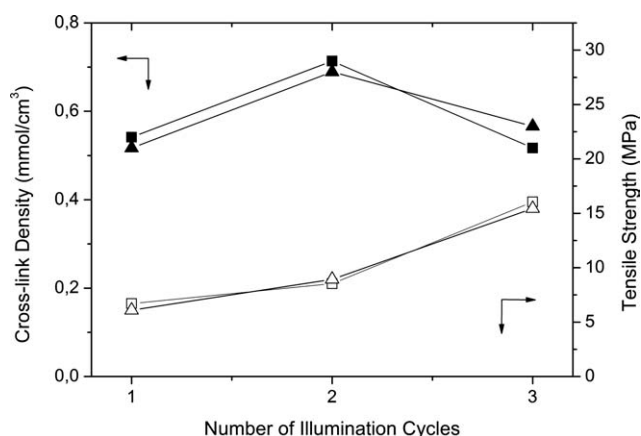
To investigate any effects of oxygen on the kinetics of the UV process and further on the tensile properties of the gloves, the prevulcanization was carried



**Figure 8** Correlation of tensile strengths (in MPa) and crosslink densities (in mmol/cm<sup>3</sup>) of nonsterile gloves prepared with 1.0 phr Genocure DMHA and 1.0 phr TriThiol using different irradiation energies.

out under inert conditions. For this experiment, the falling film reactor and the storage vessels were flooded with argon gas for 2 h. It has to be considered that oxygen is also dissolved in the latex emulsion itself, but a degassing of the reaction mixture with argon gas was not carried out due to heavy foaming.

The results in Figure 9 show that the difference in both tensile strengths and crosslink densities between air and inert conditions are negligible. Although it is well known that radical reactions often suffer from inhibition in presence of oxygen, these results give evidence that the photochemically prevulcanization is not affected by oxygen. These results are further in agreement with recent published studies dealing with the lack of oxygen sensitivity of the thiol-ene photoaddition.<sup>35</sup> Furthermore, account has to be taken into the fact that inhibition



**Figure 9** Tensile strengths (in MPa) and corresponding crosslink densities (in mmol/cm<sup>3</sup>) of nonsterile gloves photochemically prevulcanized under air and inert gas.

**TABLE III**  
**Tensile Properties of Gloves Photochemically Prevulcanized with Optimized Process Parameters After Various Treatments**

Tensile properties	Nonsterile gloves		Sterile gloves	
	Before aging	After aging	Before aging	After aging
Tensile strength (MPa)	28 ± 3	28 ± 3	26 ± 3	22 ± 3
Ultimate elongation (%)	1010 ± 20	1010 ± 20	1020 ± 30	1040 ± 30
Modulus 300% (MPa)	1.6 ± 0.2	1.6 ± 0.2	1.4 ± 0.2	1.3 ± 0.2
Modulus 500% (MPa)	3.1 ± 0.3	3.0 ± 0.3	2.9 ± 0.3	2.5 ± 0.3
Modulus 700% (MPa)	7.0 ± 0.5	6.5 ± 0.5	5.8 ± 0.5	5.2 ± 0.5

by oxygen plays an important role in the crosslinking of thin films, whereas the film thickness obtained in the falling film reactor lies in the range of millimeters.<sup>25,36</sup>

#### Effect of sterilization and aging at elevated temperature

With respect to the usage of disposable articles in the operational room such as surgical gloves, sterilization techniques play an important role to ensure the safety of the patient. Since chemical sterilization with ethylene oxide suffers from considerable drawbacks related to toxic chemical residues, the irradiation with  $\gamma$ -rays has become an appropriate sterilization technique for surgical gloves.  $\gamma$ -sterilization is carried out with a  $^{60}\text{Co}$  source and comprises a high reliability and a high degree of sterility assurance.<sup>37,38</sup> When exposing polyisoprene to high-energy radiation, scission, as well as crosslinking of the main chains can be observed. It has to be considered that in the absence of any sensitizers (e.g., monofunctional acrylic monomers), high-radiation doses (>100 kGy) are needed to achieve polymer crosslinking. However, at lower radiation doses (25 kGy) used in the sterilization of latex articles polyisoprene undergoes primarily chain scission resulting in a deterioration of the physical and mechanical properties.<sup>39,40</sup>

To evaluate the radiation stability of UV precured latex, the gloves were sterilized using a 25 kGy radiation dose. In addition, the latex gloves were aged in compliance with EN 455-2 (2000) to study the thermal and oxidative stability. According to the standard the gloves were stored at 70°C for 7 days under air.

The gloves were precured with optimized process parameters using a radiation intensity of 0.9 W/cm<sup>2</sup> and a photoinitiator (Genocure DMHA) and TriThiol concentration of 1.0 phr. The tensile properties (e.g., tensile strength, elongation at break, and modulus) of the gloves after different treatments are outlined in Table III. Comparing the tensile properties of nonsterile gloves before and after aging at 70°C, it was found that the tensile strength retains 28 ± 3 MPa.

Moreover, it was observed that the elongation at break and the moduli at 300% and 500% elongation are not significantly affected by aging. However, the exposure to a radiation dose of 25 kGy leads to a depletion of the tensile strength from 28 ± 3 to 26 ± 3 MPa which is paralleled by an increase of the ultimate elongation from 1010 ± 20 to 1020 ± 30%. A subsequent aging at 70°C results in a further decrease of the tensile strength down to 22 ± 3 MPa and an increase of the elongation at break up to 1040 ± 30%. The deterioration of the tensile properties and the thermal stability clearly indicates that chain scission occurs during  $\gamma$ -sterilization. It should be noted that the  $\gamma$ -sterilization is not carried out under inert gas atmosphere. Thus, the radiation-induced chain scission may also be followed by oxygen degradation. As a consequence, a phenolic antioxidant as radical scavenger is required to maintain high-tensile properties on aging and exposure to high-energy radiation. Although a decrease of the tensile properties is obtained due to sterilization and aging at elevated temperature, the results give evidence that UV prevulcanized surgical gloves clearly exceed the stringent quality requirements of EN 455-2 and ASTM D 3577.

#### CONCLUSIONS

Research in the field of accelerator-free crosslinking processes has been stimulated by the rising emergence of latex Type IV allergies, especially in the medical care sector. Although the feasibility of the UV prevulcanization in a falling film reactor via the thiol-ene reaction have been demonstrated in previous publications, the objective of the present study, was to detail crucial process parameters of the pilot plant.

Due to its high reactivity and absorption characteristic, Irgacure 369 as representative from the class of amino alkylphenones yields high-tensile properties (30 ± 3 MPa) but leads to colored latex products. Using Genocure DMHA as photoinitiator, yellowing can be avoided, whereas good tensile properties (28 ± 3 MPa) together with a high aging and sterilization stability are obtained. In addition, it



could be shown that trifunctional mercaptopropionate esters (crosslinker) yield to higher crosslink densities compared with tetrafunctional derivatives. Besides photoinitiator efficiency and reactivity of the components, this work has revealed that the polarity of the processing chemicals plays a key role. To ensure an efficient diffusion of the processing chemicals in the rubber particles, a low hydrophilicity of the components is required. Comparing the tensile properties of UV precure gloves with the corresponding crosslink densities, it is evident that a tighter network leads to a depletion of the tensile strength. It could be further demonstrated that the UV prevulcanization is not significantly affected by oxygen.

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