

# Energy dissipation in natural rubber latex films: The effect of stabilizers, leaching and acetone-treatment

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## Funding information

Tampere University Graduate School; Tekniikan Edistämissäätiö

## Abstract

Natural rubber (NR) is a versatile material possessing outstanding mechanical properties, which can be used in multiple applications including the rapidly developing dielectric elastomer generators (DEGs). One of the drawbacks of the existing DEGs is their low efficiency, which can be improved by lowering the dielectric and mechanical losses originating from the material. Therefore, the present research was focusing on assessing the ways to minimize the dielectric and mechanical losses of NR films rather than developing a DEG. In this article, the effect of natural proteins and the rubber stabilizers on energy dissipation of NR films was evaluated. Moreover, the effect of sample post-treatment (with water and acetone), curing and time after cure was discussed. As a result, deproteinized NR stabilized by ammonium caseinate outperformed unmodified NR due to reduced dielectric losses, mechanical hysteresis and stress relaxation. Moreover, the posttreatment methods were found to moderately reduce the material-relates losses.

## KEYWORDS

dielectric properties, elastomers, mechanical properties, rubber

## 1 | INTRODUCTION

Natural rubber (NR) is considered as a promising material for the fabrication of dielectric elastomer generators (DEGs).<sup>[1]</sup> DEGs belong to the comparably new class of energy harvesters that transform mechanical energy of an ambient source into electricity. Several DEG prototypes using commercial elastomeric materials have been successfully tested, for example, for wave energy harvesting.<sup>[1–4]</sup> However, no commercial material is specially designed for energy harvesting application and none of the currently used materials has all the required properties to make DEGs economically preferable source of electricity.<sup>[5]</sup> Apart from good mechanical properties

and low stress relaxation, material utilized for an energy harvesting application should have minimal dielectric and mechanical energy dissipation.

Generally, rubber compounding chemicals are known to affect the dielectric losses of NR. For instance, ZnO and stearic acid cause an increase in dielectric losses.<sup>[6]</sup> Moreover, some surfactants can increase dielectric losses of unvulcanized deproteinized rubber (dNR).<sup>[7]</sup> However, the effect of latex stabilizers on dielectric properties of NR and dNR has not been studied yet. From the dielectric loss point of view, natural proteins and phospholipids, as well as compounding ingredients in NR can be considered as impurities, which can increase dielectric dissipation, especially at low frequencies. The presence of

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impurities contributes to the ionic conductivity, which facilitates the increase in dielectric loss.<sup>[8]</sup> Deproteinized rubber contains about 80% less proteins than the standard NR, and the remaining proteins are much smaller in size.<sup>[9]</sup> Therefore, dNR is expected to show reduced dielectric losses without compromising the outstanding tensile properties of NR.<sup>[10,11]</sup> When compounding with an efficient vulcanization system, dNR is expected to have lower hysteresis, creep and stress relaxation.<sup>[12]</sup> Instead, the use of conventional vulcanization system has resulted in lower mechanical properties of dNR and higher mechanical energy dissipation.<sup>[13]</sup>

Although both NR latex and dNR latex,<sup>[6,7,14–16]</sup> as well as their synthetic analog polyisoprene<sup>[17–19]</sup> are well-studied in terms of their dielectric behavior, it is not clear how this property change with time. NR contains two different types of proteins: water-soluble proteins, and insoluble proteins strongly bound to the rubber molecule.<sup>[20]</sup> Water-soluble components of rubber, including some naturally occurring proteins and phospholipids, are known to migrate to the surface of a dry latex film with time.<sup>[21,22]</sup> For pre-vulcanized latexes the amount of the migrating extractable proteins are known to be considerably higher than for a post-vulcanized ones, and the amount of extractable proteins correlate with the increase in drying temperature, porosity and thickness of films. Moreover, some leaching processes may increase the amount of extractable proteins instead of decreasing it.<sup>[23]</sup> Insoluble rubber proteins are usually strongly bound to the rubber particle and are evenly distributed throughout the latex film unless they are solubilized, denaturated or degraded.<sup>[9,24]</sup> For example, washing latex with surfactants results in denaturation of proteins and eases their removal with water. Next, the use of strong alkali can hydrolyze phospholipids and degrade proteins into smaller fragments thus allowing them to be removed by washing. Application of acetone has also been found to degrade some proteins and break the established hydrogen bonds.<sup>[25]</sup> Moreover, small fragments of degraded proteins are able to create ionic linkages to the rubber particles. Therefore, not only water-soluble, but also insoluble proteins can be expected to migrate in the latex films as a consequence of a specific treatment. As the protein migration is a time-dependent process, it is important to analyze the time-dependency of the dielectric losses of the various rubber samples, also considering the effect of compounding ingredients, vulcanization process, amount of natural proteins and the posttreatment methods.

The aim of the study is to investigate the material-related losses of NR and explore their perspectives for a

DEG application by comparing them to the same properties of the most widely used commercial material – VHB4905 acrylic tape by 3 M.<sup>[1,5]</sup> The present study is focusing solely on NR-related losses (dielectric and mechanical) and the ways of their minimization rather than on the development of a DEG, as no standard DEG device or procedure is available, but the harvesting results are very much dependent on the multiple testing factors, such as device type, bias voltage, electrode type and quality, and so forth. Here, natural latex compounds, including ultra-purified NR with very low protein content are investigated in terms of energy dissipation. Moreover, the effect of stabilizers, curing time, and film posttreatment is evaluated. The aim of the study is to determine the material with low dielectric and mechanical energy losses for the potential application in DEGs. Furthermore, the study aims to identify the parameters responsible for the loss reduction. The effect of protein content reduction on dielectric losses is evaluated in rubber films by means of dielectric spectroscopy. Viscous losses of the latex films are estimated by means of dynamic mechanical analysis, cyclic loadings and stress relaxation. Soon as the effect of different compounding ingredients on the dielectric losses of NR is well-known along with the own loss contribution from the NR,<sup>[6,7,16]</sup> the study is focusing on comparing the loss behavior of the samples stabilized by KOH, which is used in the most of commercial formulations, and ammonium caseinate, which is expected to lead to the loss reduction.

## 2 | EXPERIMENTAL

### 2.1 | Materials

NR latex (Full Ammonia grade) and dNR latex (Vytex grade), both containing about 60% of polymer, were used in the study. Two different conventional latex stabilizers (KOH and ammonium caseinate) were used in compounding. Latex compounding ingredients, their roles, and suppliers are presented in Table 1. The formulation calculation is based on dry phr (parts per hundred rubber) content of the ingredients. Commercial VHB4905 acrylic adhesive tape produced by 3 M company was used for the comparison reasons. In the evaluation, compounds containing KOH stabilizer can be viewed as a reference point, as KOH stabilizer is used in the most commercial latex recipes, and preparation of the sample containing no stabilizers with the current sample preparation procedure resulted in a film with uneven surface, which was not suitable for testing.

**TABLE 1** Formulation for unfilled latex samples

Ingredient	Supplier	Role	Amount, phr-dry			
			NR_KOH	dNR_KOH	NR_a.c.	dNR_a.c.
Full ammonia NR latex	Centrotrade Deutschland	Elastomer	100	–	100	–
Deproteinized NR latex			–	100	–	100
KOH 1 N	VWR	Stabilizer	0.1	0.1	–	–
Ammonium caseinate	Akron		–	–	0.5	0.5
Zinc dibutyldithiocarbamate (ZDBC)		Accelerator	2	2	2	2
Sulfur		Curative	1	1	1	1
ZnO	Sigma Aldrich	Activator	1	1	1	1

## 2.2 | Sample preparation

Latex was mixed with curatives by magnetic stirrer. The obtained solutions were poured into the molds, degassed in vacuum for 30 min and left for 24 hr for drying. The dried samples were gently removed from the molds and cured in the ventilated oven at 120°C for 15 and for 30 min. Leaching treatments were performed on dried unvulcanized samples by washing in deionized water at 35°C for 20 min. The samples were vulcanized after drying at room temperature for 24 hr. Acetone treatment was performed on vulcanized samples by immersing them into acetone for 30 min at room temperature. After the treatment, the samples were washed in deionized water and dried for 24 hr at room temperature.

## 2.3 | Testing methods

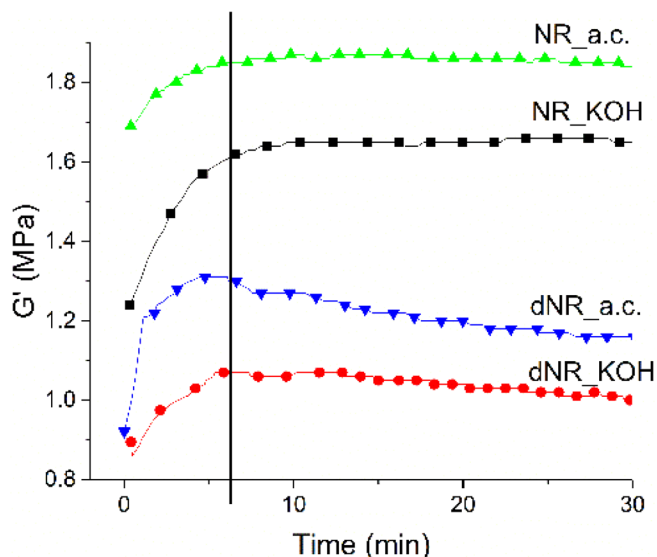
Stains can be applied to visualize mostly water-soluble proteins on the surface of a rubber film, and the relative protein content can be estimated from the resulting change in color.<sup>[21]</sup> However, such method cannot be correlated to the absolute quantity of the proteins, and also may include some of the insoluble rubber proteins.<sup>[26]</sup> Staining was performed on dry latex samples by immersing them in amido-black staining solution (Sigma Aldrich) for 2 min, blotting the samples dry and de-staining for 30 min in acetic acid/isopropanol/water solution (10/25/65% by volume). The de-staining solution removes all unreacted stain. The colorimetric analysis was performed with (Minolta CR-300) in the  $L^*ab$  scale, where color is expressed as three numerical values:  $L^*$  for the lightness,  $a^*$  and  $b^*$  for the green–red and blue–yellow color components. Difference between colors before and after the staining  $\Delta E_{ab}^*$  was calculated based on formula (1):

$$\Delta E_{ab}^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}, \quad (1)$$

where index 1 stands for an unstained sample, and index 2 for the stained one. Due to their transparency, all the samples were evaluated against white background. Three parallel measurements were conducted, and the average value reported.

Curing characteristics of the materials were studied with DMA 861e (Mettler Toledo). Uncured samples were tested in shear mode at 120°C and 1 Hz frequency for 30 min, and the change in shear modulus was recorded. Temperature pre-equilibration step took 8 min before the actual test. The optimum curing time was determined at the maximum modulus value. However, as the temperature equilibration stage took place before the actual measurement, that time was added. For the samples, the optimum curing time was determined as about  $7 + 8 = 15$  min. It was also noticed from Figure 1 that dNR samples showed some reversion—decrease in modulus after the optimum curing was reached, which is related to the breakage of some sulfur bonds. Reversion is common for the NR compounds, and in this case can be related to the decreased amount of proteins.<sup>[27]</sup>

Dynamic mechanical analysis (DMA) and cyclic loading of the samples were performed with Pyris Diamond DMA (Perkin Elmer) using the 1 mm thick samples. DMA samples were measured in the tension mode at 1 Hz with 0.1% displacement amplitude and 3°C/min heating rate. For the stress relaxation measurement, samples were stretched to 10% and the change in force was recorded. The determination of moduli and tensile cyclic loading was performed on Z1.0 tensile testing machine (Zwick/Roell) at ambient conditions at 500 mm/min rate and 100% maximum elongation. The test length was 35 mm. Prestress of 0.1 N was applied to avoid buckling of the samples. Three specimens of each sample were tested, and the average value was calculated. The hystere-



**FIGURE 1** DMA storage modulus of the latex films during curing at 120°C. The temperature stabilization prior to the measurement (8 min) is not shown in the graph [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

sis loss was calculated by subtracting integrated loading and unloading curves and dividing the value by the area under the corresponding loading curves. Three specimens of each sample were tested, and the average value was reported.

Dielectric permittivity, dielectric loss and electrical conductivity were measured with a Novocontrol Alpha-A dielectric analyzer. The tests were conducted at room temperature ( $23 \pm 1^\circ\text{C}$ ) and relative humidity  $35 \pm 3\%$ . The frequency sweep was done from 0.5 Hz to 1 MHz. Samples were placed between 2 mm thick rigid gold-plated electrodes 20 mm in diameter. Both samples and electrodes were wiped with isopropanol prior to the test to remove any impurities from the surface, improve the contact between the sample and electrodes thus reducing possible electrode polarization. The dielectric response of the samples was obtained as complex permittivity  $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ , where  $\omega = 2\pi f$  is the angular frequency,  $\epsilon'$  is the real part of the complex dielectric permittivity and  $\epsilon''$  is the imaginary part—dielectric loss. Moreover, the electrical conductivity of the samples was measured. Three specimens of each sample were tested, and the average value was calculated.

Fourier transform infrared spectra (FTIR) was obtained with Bruker Tensor 27 in the attenuated total reflectance (ATR) mode in the range from 500 to  $4,000\text{ cm}^{-1}$  with a diamond crystal background and  $4\text{ cm}^{-1}$  resolution. The apparent crosslink densities  $1/Q$  was calculated from the swelling values  $Q$  (Equation (2)),

which is defined as grams of solvent per gram of rubber hydrocarbon<sup>[28]</sup>:

$$Q = \left( \frac{m_s - m_d}{m_0} \right) \frac{F}{100}, \quad (2)$$

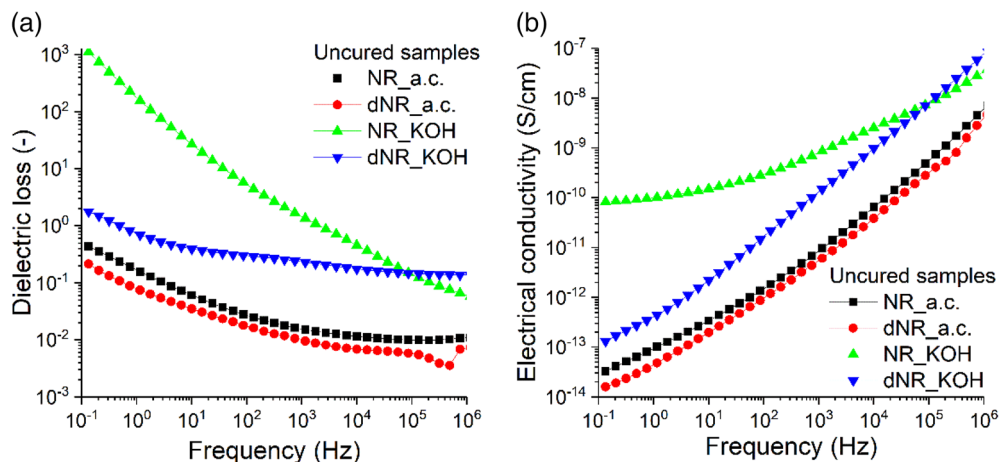
where  $m_s$  and  $m_d$  are the weight of the swollen and dried specimen respectively,  $m_0$  the initial weight of the sample, and  $F$  is formula weight, meaning total weight of rubber together with compounding ingredients based on 100 parts of rubber. For the determination of apparent crosslink density, three specimens (10x10 mm) of the sample were weighed and then immersed in toluene for 72 hr. The solvent was renewed every 24 hr. The saturated swollen specimens were removed from solvent, wiped quickly with filter paper and weighed. Specimens were weighed again after 48 hr drying in air. Three parallel measurements were conducted and the average values were reported.

### 3 | RESULTS AND DISCUSSIONS

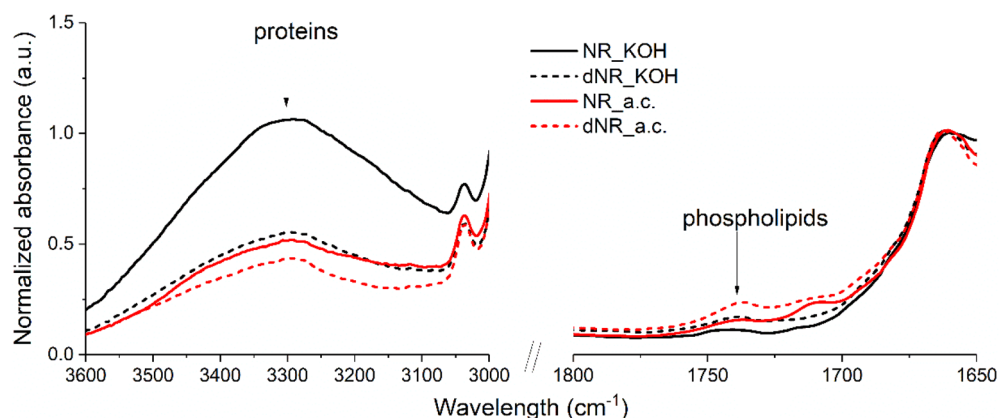
#### 3.1 | Uncured samples

The dielectric loss curves of uncured NR and dNR samples containing either KOH or ammonium caseinate stabilizer are presented in Figure 2a. The compounds stabilized by KOH show very high dielectric losses compared to the samples compounded with ammonium caseinate. Increased dielectric losses at low frequencies can usually originate from the parasitic electrode polarization, the contribution from electrical conductivity or the interfacial (Maxwell-Wagner) polarization.<sup>[29]</sup> Electrode polarization is always expected in the samples with ionic conductivity, and it often overlaps with the effect from conductivity contribution. The conductivity effect contributing to the dielectric loss is usually seen from the slope of dielectric loss linearly increasing towards lower frequencies and from the increased electrical conductivity in the same frequency area. According to the changing slope of dielectric loss plot of NR\_KOH shown in Figure 2a, both electrode polarization and the conductivity contribution were responsible for the high losses. Moreover, as can be seen from the electrical conductivity graph presented in Figure 2b, the samples containing KOH are much more electrically conductive than the corresponding samples containing ammonium caseinate stabilizer. The presence of proteins in a dry film should not cause such dielectric behavior.<sup>[30]</sup> Instead, the increased electrical conductivity and dielectric losses can be explained by the effect of mobile ions, which originate

**FIGURE 2** (a) Dielectric loss; and (b) electrical conductivity plot of unvulcanized rubber samples with different stabilizers [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**FIGURE 3** Normalized FTIR spectra of NR and dNR samples with different stabilizers. dNR, deproteinized rubber; FTIR, Fourier transform infrared spectra; Nr, Natural rubber [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



from the additives (e.g., KOH) and the fragments of degraded proteins upon addition of KOH stabilizer.

According to Chaikumpollert et al.,<sup>[10]</sup> FTIR absorption peaks at  $3300\text{ cm}^{-1}$  ( $-\text{OH}$ ) and  $1739\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  ester stretching) can be characteristic for the natural proteins and phospholipids in NR, respectively. In order to compare the relative amounts of proteins and phospholipids, the corresponding peak intensities were normalized by dividing by the intensity of a reference peak  $1,664\text{ cm}^{-1}$  ( $\text{C}=\text{C}$ ) originating from the polyisoprene chain.<sup>[10,31]</sup> Based on the normalized FTIR spectra shown in Figure 3, samples containing KOH stabilizer are expected to have more proteins and less phospholipids on the surface, but it can be overestimation, as KOH adds to the concentration of  $-\text{OH}$  group. Moreover, addition of KOH can cause denaturation of some proteins and alkaline hydrolysis of lipids, similarly to the saponification process,<sup>[13]</sup> which results in increased  $-\text{OH}$  amount and decreased  $\text{C}=\text{O}$  ester stretching peak.<sup>[32]</sup> KOH can even be used in the posttreatment method for removing the proteins from NR samples.<sup>[33]</sup> According to the normalized FTIR spectra shown in Figure 3, dNR\_a.c. containing

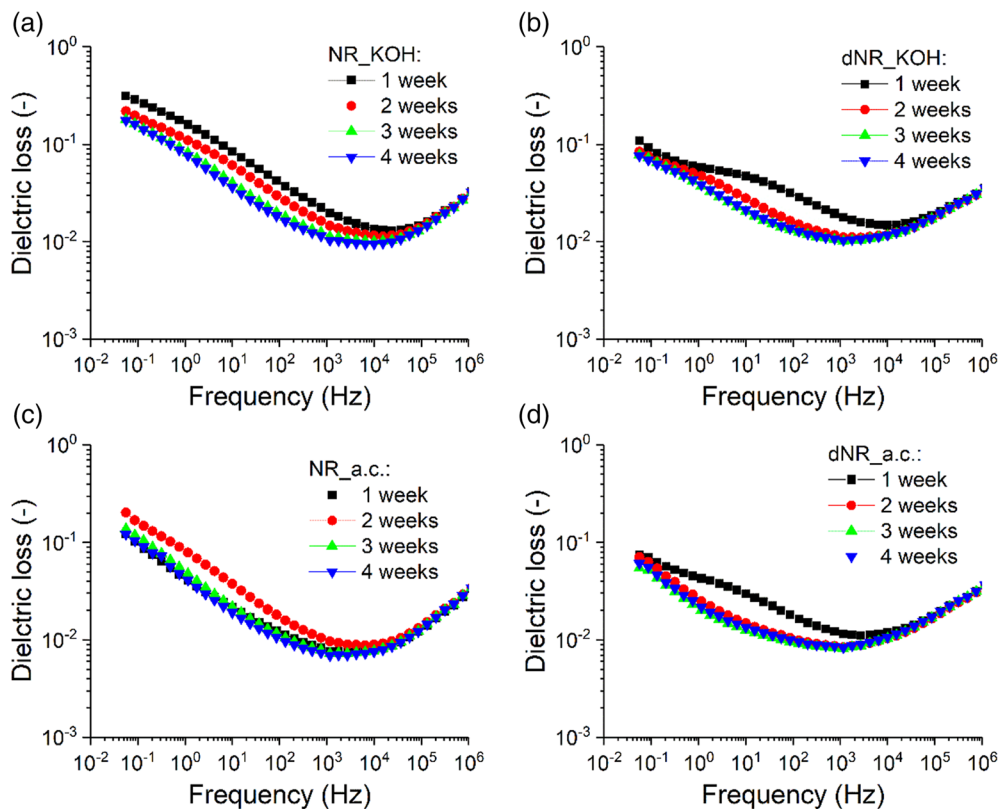
ammonia caseinate had the lowest amount of proteins, but the highest content of phospholipids. NR\_KOH showed the highest protein-associated peak, and it is expected to have a large amount of proteins. This could suggest a pronounced increase in dielectric losses.

When discussing water-soluble surface proteins, staining reveals that freshly prepared uncured samples with added ammonium caseinate have higher concentration of proteins on the surface than the samples containing KOH (Table 2). Moreover, dNR has less surface proteins compared to NR. Indeed, ammonium caseinate is a protein-based stabilizer, and the staining method is unable to distinguish between the specific protein types. Moreover, this staining method should not reveal insoluble proteins on the rubber particle surface, but may give a little color change due to their presence,<sup>[21]</sup> as seen in case of dNR\_KOH sample. Together with the effect of KOH, this can explain the difference in protein evaluation by FTIR and colorimetry. In the colorimetric method, the stain reacted with the water-soluble proteins and with the added ammonium caseinate stabilizer on the surface of the latex film.



**TABLE 2** Apparent crosslink density and colorimetric data of the unvulcanized rubber samples

Property	NR_KOH	dNR_KOH	NR_a.c.	dNR_a.c.
Apparent crosslink density (1/Q), –	0.056 ± 0.023	0.069 ± 0.001	0.044 ± 0.005	0.100 ± 0.003
Color difference ( $\Delta E^*_{ab}$ ), –	10.1 ± 0.5	5.5 ± 0.4	21.0 ± 0.5	12.0 ± 0.5

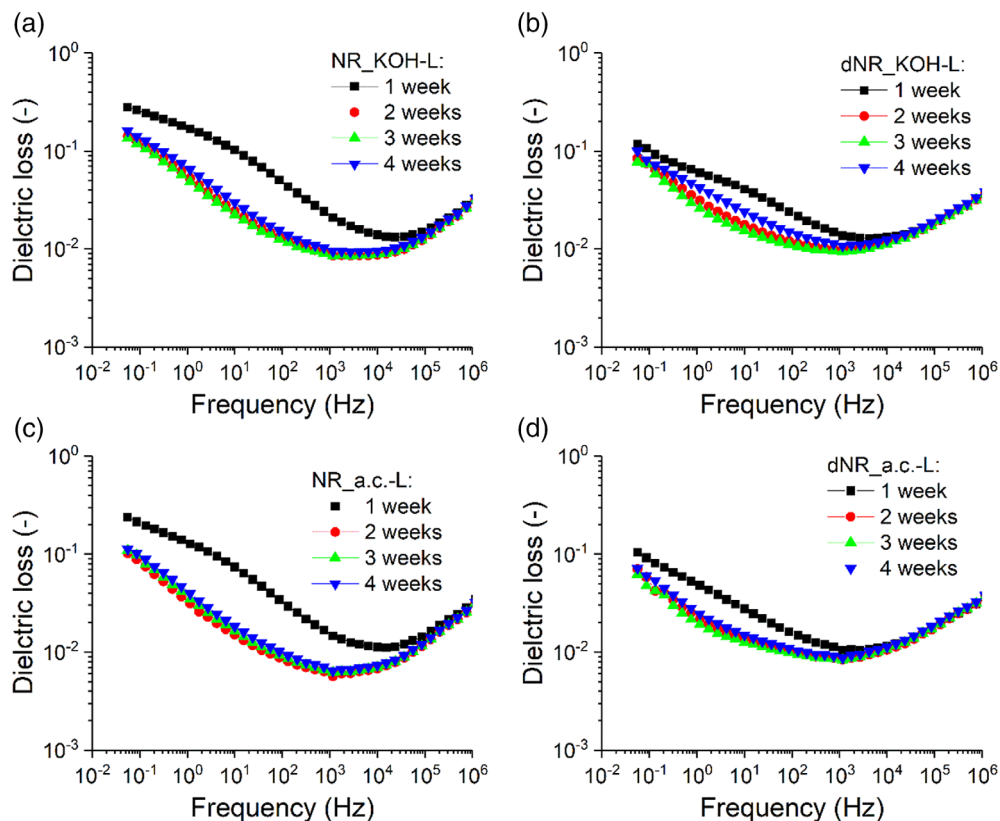
**FIGURE 4** Time-dependency of dielectric loss properties of (a, c) NR and (b, d) deproteinized NR films cured for 15 min. Nr, Natural rubber [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

Different compounding ingredients affect the crosslinking properties of the materials as well. As can be seen from the Table 2, even unvulcanized samples have certain degree of crosslinking. The effect is partly explained by the developing branching points due to the presence of proteins and/or phospholipids.<sup>[34]</sup> Moreover, as the samples are compounded with the curatives, even at room temperature the curing process proceeds slowly during the film drying process.<sup>[35]</sup> The high crosslinking and deviation of NR\_KOH over NR\_a.c. can be explained by the ability of the protein fragments appeared due to the addition of strong alkali to link to the  $\omega$ -terminals in NR chain.<sup>[9]</sup> Surprisingly, unvulcanized dNR shows the highest 1/Q among the samples. The explanation may be that due to the largely reduced amount of the proteins on the rubber particle surface, the compounding ingredients and the stabilizers were adsorbed to the surface more readily. Ammonium caseinate can serve as an accelerator due to the presence of ammonia ion, which may explain high 1/Q of the dNR\_a.c. sample.

### 3.2 | Time dependency of dielectric properties

Although no standard procedures are available specifically for dielectric elastomer transducers, Carpi et al.<sup>[36]</sup> developed a set of recommendations aiming to make the testing results comparable within the field of application. In the document, much attention is paid to the effect of sample thickness, selection of electrodes and testing conditions, such as temperature, humidity, strain level and voltage. However, no recommendation about the effect of time after curing and the curing conditions have been mentioned. As a common practice, for example, for the tensile tests ISO 37 and electrical resistivity tests ASTM D991, testing of rubber materials is performed between 16 hr and 4 weeks after vulcanization. However, it was noticed in the present and previous study<sup>[37]</sup> that the dielectric loss properties of some rubbers could change a lot during this timeframe. Moreover, the extent of the change in dielectric losses with time depends on curing

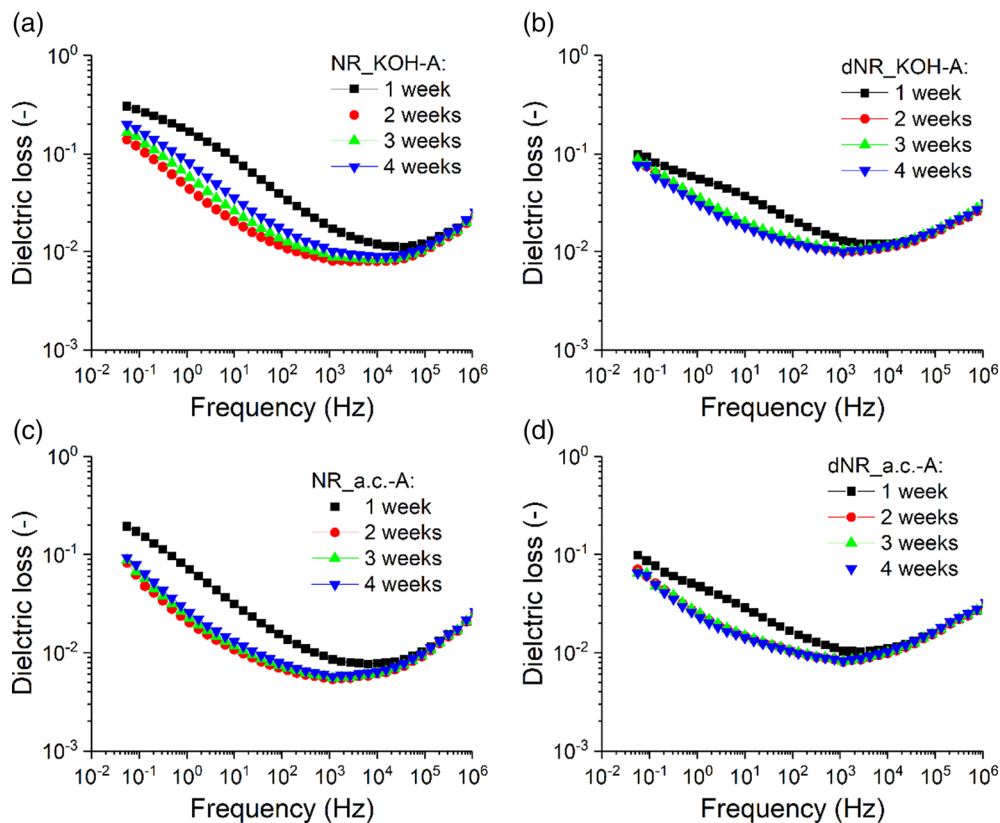
**FIGURE 5** Time-dependency of dielectric losses of water-leached (a, c) NR and (b, d) deproteinized NR films cured for 15 min. Nr, Natural rubber [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



time of the compounds, and consequently the crosslink densities. Finally, the type of a stabilizer and different post-treatment methods play a role in changing the dielectric properties of the compounds. Therefore, it is important to study the dependency of dielectric loss on time after curing and evaluate the possible cause of such change in order to determine the optimum time intervals for the testing.

Similarly to the uncured samples, dielectric losses of samples containing KOH were a little higher than of the samples containing ammonium caseinate stabilizer, as seen from Figure 4, showing the change of the dielectric losses depending on the time after cure. At room temperature, the increase in dielectric loss above  $10^4$  Hz is associated with the segmental dynamics of NR ( $\alpha$ -relaxation).<sup>[15]</sup> It is seen that changes in dielectric loss with time are observed below  $10^4$ – $10^5$  Hz, which, therefore, implies the changes are not related to the polymer network or chain dynamics. According to the shapes of the curves, the reason for increased loss is a pronounced interfacial polarization combined with the conductivity contribution. Contribution from the electrical conductivity is seen at the linear portion of the loss curve at frequencies below 1 Hz,<sup>[29]</sup> after which interfacial polarization with its peak in the range 10–100 Hz adds up to the total dielectric losses. Interfacial polarization also known as Maxwell-Warner polarization arises from dielectric and electrical differences at the interface

between the elastomer and filler particles resulting in a charge build-up. In compounded NR, ZnO is most often responsible for such polarization effect,<sup>[6]</sup> but proteins and different impurities can be another reason for the interfacial polarization. The interfacial polarization is also associated with the small increase in dielectric permittivity starting at the peak frequency. In Figure S1, dielectric permittivity shows the most increase for the NR samples, and the presence of KOH stabilizer results in higher permittivity gain at low frequency than in case of ammonium caseinate stabilizer. As all the samples contain the same amount of ZnO, the reason for the differences in the interfacial effect can be proteins or time-dependent decomposition of ZDBC accelerator, which is more pronounced for the dNR samples.<sup>[38]</sup> Moreover, the effect of proteins possibly denaturated by KOH is more pronounced. The contribution of electrical conductivity can be confirmed for all the samples by looking at the electrical conductivity plot shown in Figure S2. It can be seen that deproteinized dNR samples show less change in electrical conductivity at low frequency than the NR samples. Based on the observations, time-dependency of the dielectric losses can be related to the migration of free ions and proteins. Therefore, based on the analyzed dielectric data, it is recommended to perform dielectric tests between 2 and 4 weeks after curing the latex, as the dielectric properties seem to stabilize at that point.



**FIGURE 6** Time-dependency of dielectric loss properties of acetone-treated (a, c) NR and (b, d) deproteinized NR films cured for 15 min. Nr, Natural rubber [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

As a part of the proteins in NR is water-soluble, including added ammonium caseinate, leaching latex films with water helps to remove a part of the proteins together with water-soluble compounding ingredients unused during the vulcanization. In leached NR samples, significant difference in dielectric losses was seen between 1 and 2 weeks after cure, then the losses stabilized, as shown in Figure 5. Deproteinized rubber also showed reduction in losses between 1 and 2 weeks, but the difference was very small compared to the NR samples. Moreover, the NR samples showed more significant reduction of the dielectric losses associated with electrical conductivity, while the contribution of interfacial polarization seems to be the same as for untreated samples. As leaching showed no significant effect on the dNR samples, water-extractable proteins are expected to be partly responsible for the time-dependency of the samples. Furthermore, as leaching facilitates the removal of free ions, small reduction in losses between treated and untreated samples can be related to the presence of ions contributing to the conductivity of the material.

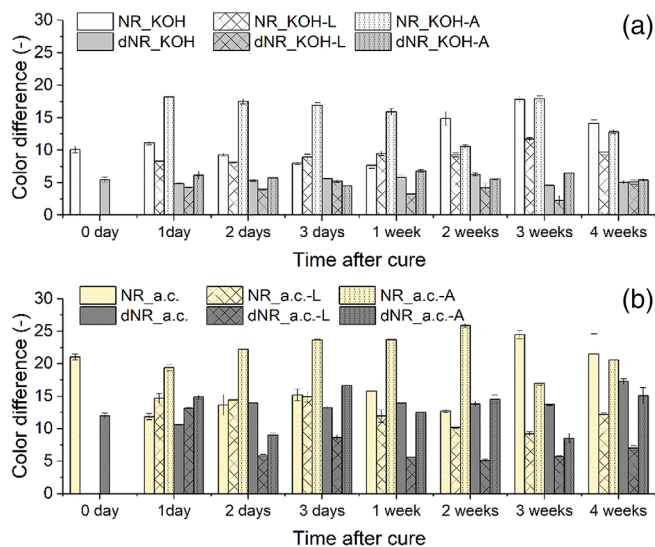
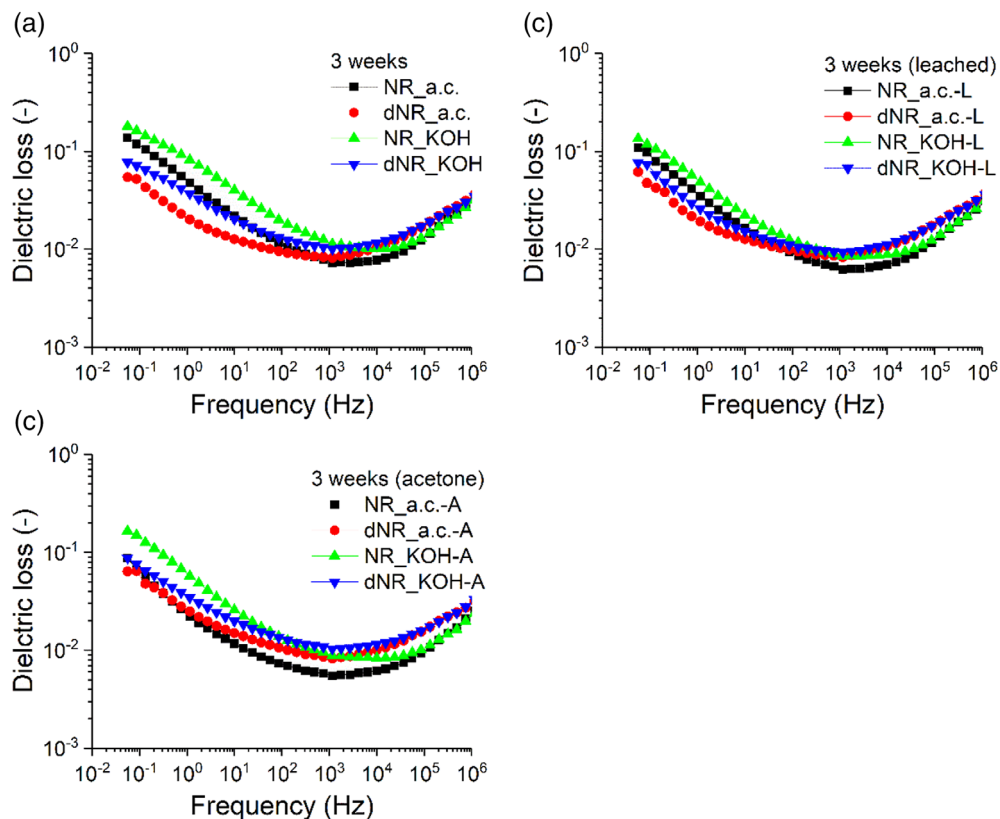
The portion of natural proteins insoluble in water can be extracted by the acetone-treatment. Some unvulcanized rubber chains can also be dissolved during this treatment. According to the Figure 6, acetone-treated samples show similar loss pattern as untreated samples,

except for the NR\_a.c. samples, which show lower dielectric losses in the low frequency range. Therefore, as theoretically expected, acetone interacts with insoluble proteins of natural rubber rather than hydrolyzed or denaturated proteins.

As the result of dielectric tests at different times after vulcanization, the dielectric properties of the samples can be considered as stabilized when measured at 3 weeks after cure. The stabilized dielectric losses of the compounds are compared in Figure 7 in terms of the rubber and stabilizer types as well as the posttreatment methods. The compounds containing KOH stabilizer showed generally higher dielectric losses at frequencies below 10 Hz than the compounds containing ammonium caseinate. Moreover, as expected, the losses of deproteinized dNR were lower than the standard NR. Leaching led to small reduction of dielectric losses not affecting the dNR\_a.c. sample, which is low in protein and contains no KOH. Moreover, as the shapes of the curves of KOH-containing samples change due to leaching, the samples could have some KOH-modified proteins that were removed by leaching. At the same time, acetone-treatment seemed to be successful only in reducing the dielectric losses of the NR\_a.c. This can be related to the ability of acetone to remove the insoluble proteins.<sup>[33]</sup> The presence of KOH stabilizer could have affected the structure of the proteins



**FIGURE 7** Comparison of the stable dielectric losses of (a) untreated; (b) leached; and (c) acetone-treated rubber samples [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 8** Changes in colorimetric data of the post-treated samples containing (a) KOH; and (b) ammonium caseinate stabilizer with time. Time scale is based on the curing moment of the untreated samples [Color figure can be viewed at wileyonlinelibrary.com]

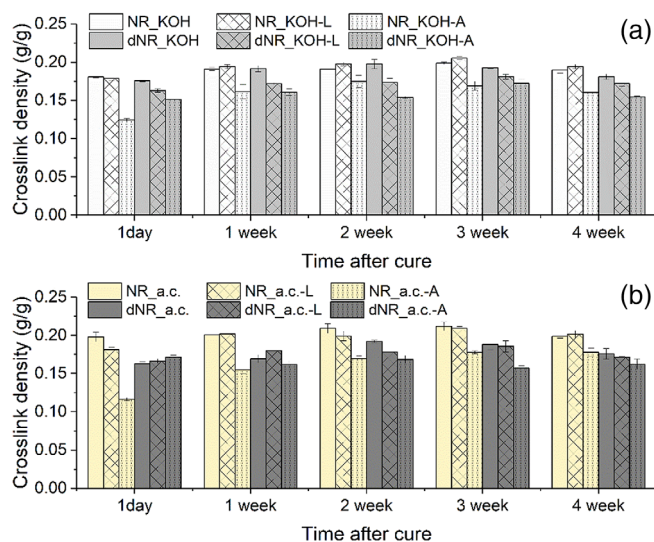
making them less extractable by the acetone. This can explain the smaller amount of surface proteins revealed by the staining between the samples containing KOH and ammonium caseinate stabilizer (Figure 8).

Regardless of the posttreatment, the dNR\_a.c. samples had the lowest dielectric loss at low frequencies.

According to the colorimetry results at different times after cure presented in Figure 8, the untreated samples containing ammonium caseinate had higher content of the surface proteins compared to KOH-stabilized compound. As the uncured NR\_a.c. sample showed almost twice higher color difference than at 1 day after cure (Figure 8b), most of the protein-containing stabilizer was expected to be migrated to the surface during the film drying phase. Thus, the increase in color difference seen in the NR\_KOH and the NR\_a.c. at 3 weeks after cure can be related to the migration of the natural proteins. The finding is also consistent with the dielectric data, where the minimum losses were achieved after 2 weeks after curing. At the same time, dNR samples show little dependence on time regardless of the stabilizer type. Moreover, leaching was an efficient method to reduce the amount of water-soluble proteins in all the samples, and these samples showed little dependency of the protein content on time after cure, same as the dielectric changes over time after cure were small. The acetone treatment of all NR samples resulted in significantly increased  $\Delta E_{ab}^*$ , as can be seen from the Figure 8. Acetone is known to cause denaturation and precipitation of proteins, probably allowing extracting some insoluble proteins from the bulk of the sample to the surface, where they can be

detected by colorimetric method.<sup>[39]</sup> Moreover, acetone can dissolve a small portion of rubber thus exposing rubber from under the surface. Acetone treatment was found to have very little effect on the deproteinized rubber samples, which can be related to the reduced amount of insoluble rubber proteins available for the acetone extraction, which is consistent with the dielectric data results.

In order to estimate, if the changes in dielectric loss can be related to the degree of crosslinking of the samples, the apparent crosslink densities were compared at different times after cure. It became evident that crosslinking continued developing a little with time. However, as seen from Figure 9, the change was minor

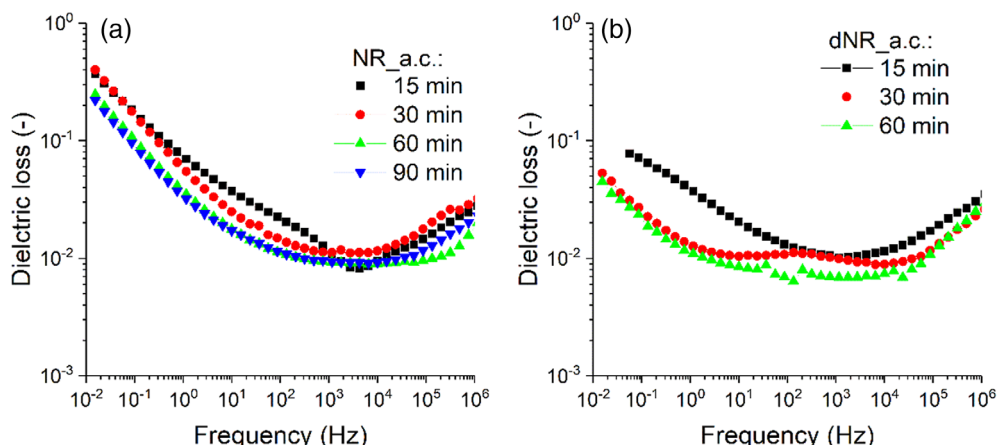


**FIGURE 9** Apparent crosslink densities of the samples stabilized with (a) KOH; and (b) ammonium caseinate depending on the time after cure [Color figure can be viewed at [wileyonlinelibrary.com](#)]

and could not be responsible for the more significant change in dielectric losses. As expected, dNR samples had somewhat lower crosslink densities due to the reduced amount of natural proteins that can create branching points and may serve as cure activators.<sup>[40]</sup> Addition of ammonia caseinate, compared to KOH, increased the apparent crosslink density of NR samples a little, but decreased the apparent crosslink density of dNR. The effect on NR samples can be explained by the accelerating effect of the stabilizer containing ammonia, which is more consumed by surface of deproteinized latex particles making it less available during the curing. Acetone treatment decreased the apparent crosslink density of the NR compounds regardless of the NR stabilizer type. As acetone cannot break the crosslink created during the vulcanization process, the results can be explained by elimination of the crosslinking points related to the protein interactions. As these proteins are not connected to the NR chains, they are expected to be prone to migration, which is confirmed by the high surface protein concentration of the same compounds. This also explains little effect of the acetone-treatment on the dNR\_a.c. samples.

**TABLE 3** Crosslink densities versus curing time of the compounds containing ammonium caseinate stabilizer

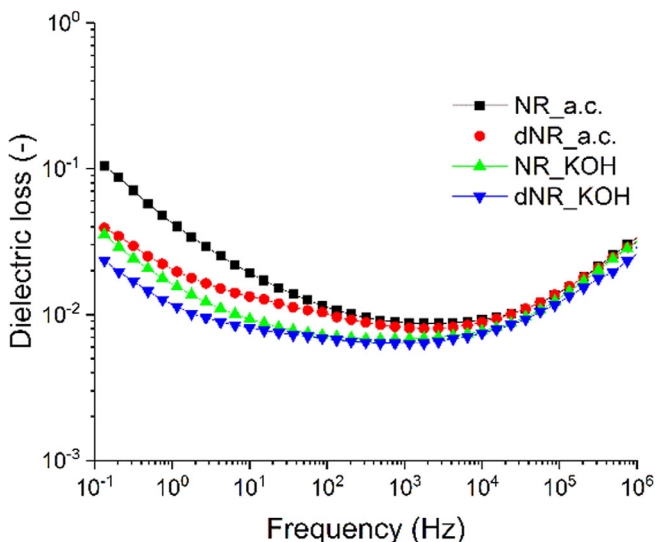
Curing time, min	Apparent crosslink density $1/Q$ , g/g	
	NR_a.c.	dNR_a.c.
0	$0.066 \pm 0.015$	$0.072 \pm 0.001$
15	$0.201 \pm 0.001$	$0.169 \pm 0.005$
30	$0.241 \pm 0.005$	$0.195 \pm 0.001$
60	$0.225 \pm 0.001$	$0.178 \pm 0.003$



**FIGURE 10** Dielectric loss of (a) NR; and (b) dNR samples stabilized with ammonium caseinate depending on the curing time. Nr, Natural rubber [Color figure can be viewed at [wileyonlinelibrary.com](#)]

### 3.3 | Dielectric and mechanical energy dissipation

It was found that the dielectric loss of the samples cured for 15 min could be comparably high even for the samples stabilized with ammonium caseinate. Moreover, the posttreatment methods reduced the dielectric losses less than expected. Therefore, dielectric properties in the low frequency region were compared depending on the curing time for the NR\_a.c. and dNR\_a.c. samples, which



**FIGURE 11** Dielectric losses of the rubber samples cured for 30 min [Color figure can be viewed at wileyonlinelibrary.com]

originally showed lower dielectric losses than KOH containing compounds. The dependence of dielectric loss on curing time is shown in Figure 10. Dielectric loss at low frequencies decreased with an increase in curing time until the equilibrium was reached. The effect is most likely related to the growing polymer network, which decreased the mobility of large protein molecules. As can be seen from the crosslink densities of the compounds cured for different times (Table 3), the maximum degree of crosslinking was reached at 30 min curing, after which the amount of crosslinks started degrading. Therefore, together with lower dielectric properties, materials cured for 30 min were expected to have optimum mechanical properties.

When comparing the equilibrium dielectric properties of rubbers cured for 30 min and containing different stabilizers in Figure 11, one can notice that dielectric losses were reduced for all the samples compared with the rubber cured for 15 min. The most pronounced decrease in dielectric losses was shown by the samples stabilized with KOH, while the loss reduction of the samples stabilized with ammonium caseinate was not that significant.

Due to the lower dielectric losses, samples cured for 30 min were chosen for further mechanical testing in order to evaluate the mechanical energy dissipation through the cyclic hysteresis loss and stress relaxation, which are important considering the possible application of such materials in DEG. Moreover, the tensile moduli at 10, 50, and 100% elongation were evaluated in order to estimate the effect of different sample constituents.

**TABLE 4** Modulus values

Sample	Modulus, MPa								
	10%			50%			100%		
	–	Leach	Acetone	–	Leach	Acetone	–	Leach	Acetone
NR_KOH	0.12 ± <0.01	0.12 ± <0.01	0.12 ± 0.01	0.37 ± 0.01	0.39 ± <0.01	0.37 ± 0.01	0.52 ± 0.02	0.55 ± 0.01	0.52 ± 0.02
dNR_KOH	0.12 ± 0.01	0.13 ± <0.01	0.12 ± 0.01	0.36 ± 0.02	0.40 ± 0.01	0.39 ± 0.02	0.51 ± 0.03	0.58 ± 0.01	0.55 ± 0.03
NR_a.c.	0.13 ± <0.01	0.14 ± <0.01	0.13 ± <0.01	0.46 ± 0.01	0.46 ± 0.01	0.39 ± <0.01	0.55 ± 0.01	0.66 ± 0.01	0.54 ± 0.01
dNR_a.c.	0.13 ± <0.01	0.12 ± <0.01	0.12 ± 0.01	0.39 ± 0.02	0.39 ± 0.01	0.37 ± 0.03	0.55 ± 0.03	0.56 ± 0.02	0.53 ± 0.04

**TABLE 5** DMA numerical results

Sample	Temperature at $\tan \delta_{\max}$ , °C			$\tan \delta_{\max}$ , –			$\tan \delta$ at 20°C, –		
	–	Leach	Acetone	–	Leach	Acetone	–	Leach	Acetone
NR_KOH	–53.5	–54.7	–55.0	1.94	2.42	2.15	0.076	0.067	0.076
dNR_KOH	–55.7	–54.5	–55.5	2.41	2.40	2.43	0.084	0.069	0.082
NR_a.c.	–55.9	–56.2	–57.6	2.29	2.36	2.25	0.073	0.079	0.083
dNR_a.c.	–56.9	–55.1	–55.7	2.33	2.42	2.45	0.106	0.085	0.092

**TABLE 6** Hysteresis loss  $\Delta H$  of the latex compounds

Sample	$\Delta H$ at 1st cycle, %			$\Delta H$ at 10th cycle, %		
	–	Leach	Acetone	–	Leach	Acetone
NR_KOH	19.2 ± 1.4	16.4 ± 1.3	17.9 ± 0.2	9.1 ± 0.5	7.2 ± 0.4	7.0 ± 0.2
dNR_KOH	19.3 ± 1.4	16.3 ± 0.8	16.1 ± 0.6	7.9 ± 0.3	5.7 ± 0.2	6.7 ± 0.2
NR_a.c.	19.2 ± 1.9	14.1 ± 0.7	16.7 ± 1.7	9.1 ± 0.1	5.6 ± 0.5	7.8 ± 0.8
dNR_a.c.	16.3 ± 1.7	16.4 ± 1.8	16.2 ± 1.1	7.1 ± 1.0	6.3 ± 0.3	6.1 ± 0.1

**TABLE 7** Stress relaxation of the latex compounds

Sample	Stress loss at 1 min, %			Stress loss at 5 min, %			Stress loss at 60 min, %		
	–	Leach	Acetone	–	Leach	Acetone	–	Leach	Acetone
NR_KOH	5.8 ± 0.3	5.3 ± 1.4	4.0 ± 0.6	9.7 ± 1.4	9.4 ± 2.1	6.8 ± 0.7	13.3 ± 1.9	13.1 ± 2.1	10.3 ± 1.0
dNR_KOH	4.9 ± 1.2	4.1 ± 0.6	4.1 ± 0.5	7.5 ± 0.9	7.1 ± 1.4	7.2 ± 2.5	10.4 ± 0.7	10.4 ± 1.8	10.4 ± 3.3
NR_a.c.	5.6 ± 1.9	4.4 ± 1.1	4.2 ± 0.4	10.1 ± 1.8	7.6 ± 1.5	6.7 ± 1.1	13.8 ± 1.6	10.6 ± 2.9	9.5 ± 2.2
dNR_a.c.	3.6 ± 1.1	4.2 ± 0.6	3.8 ± 0.1	5.9 ± 1.9	6.7 ± 1.1	5.9 ± 0.2	8.0 ± 2.2	9.1 ± 2.6	8.4 ± 0.2

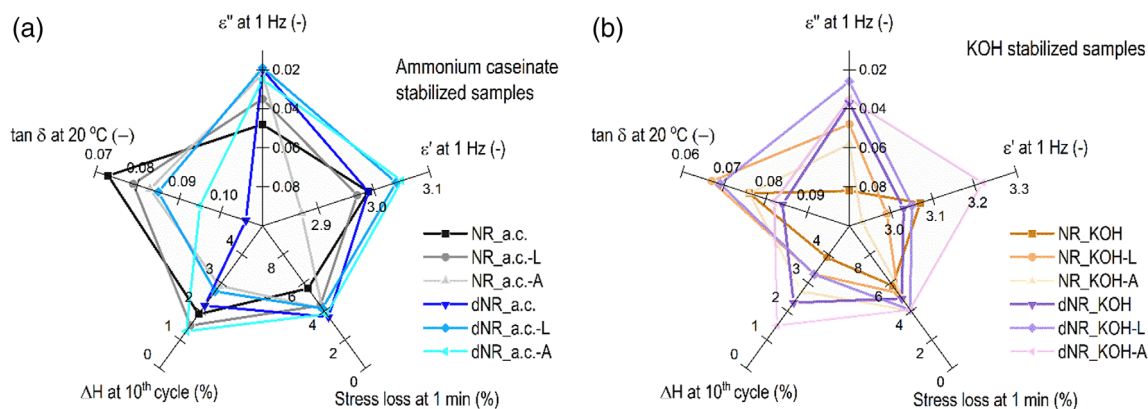
According to Table 4, the difference between NR and deproteinized dNR is minimal, as was expected. Leaching may cause some increase in moduli, especially in NR samples and KOH-containing rubber.<sup>[38]</sup> Acetone-treatment resulted in a small decrease of moduli, which can be related to the removal of some rubber-protein bonds. Moreover, the effect of posttreatment on molecular dynamics and energy damping can be evaluated by means of dynamic mechanical analysis (DMA). The energy damping is expressed as loss tangent ( $\tan \delta$ ) which is the ratio of elastic modulus  $E'$  to the loss modulus  $E''$ . The glass transition temperature  $T_g$  determined at maximum loss tangent (Table 5) indicated that dNR samples have more chain mobility, which is probably related to less proteins interacting with the rubber. While leaching seems not to cause significant changes in the chain mobility, the acetone-treatment reduced the  $T_g$  of NR compounds much more. This may mean that some rubber-associated proteins were removed from the system upon the treatment, rubber-protein linkages were broken thus giving more freedom to the rubber chains. However, the changes in  $T_g$  are still small. Furthermore, NR samples showed lower maximum values of  $\tan \delta$  than dNR samples, indicating that the motion of the molecules is more restricted, for example, due to the presence of the proteins.

Energy damping during the DEG application can be estimated by the  $\tan \delta$  value at 20°C. It can be seen that NR samples show the least energy dissipation, which can be attributed to the more restricted network. The dNR samples, instead, had the highest  $\tan \delta$  loss at 20°C,

which was reduced by leaching. As leaching seems not to affect the NR samples much, the effect is related to the elimination of the small particles contributing to the friction rather than water-soluble proteins. Acetone-treatment affected only samples containing ammonium caseinate. In the NR\_a.c. sample the treatment increases the chain mobility which causes more energy dissipation, while in the dNR\_KOH sample it decreased the loss.

Mechanical hysteresis loss ( $\Delta H$ ) describes the energy lost during the loading-unloading cycle, which is a common source of the energy dissipation in DEGs. Rubbers experience hysteresis due to their viscoelastic nature. Moreover, the first several cycles always show higher hysteresis loss due to the Mullins effect related to the slipping and rearrangement of the rubber chains along each other and the filler particles. Therefore, hysteresis losses of the compounds are evaluated at 1st and at 10th cycle. As expected,  $\Delta H$  was much higher at the first cycle than at the 10th cycle for all the compounds but leaching efficiently reduced hysteresis losses in all cases except for the dNR\_a.c., as can be seen in Table 6. This implies that the sample is poor in water-extractable proteins. The most effect of leaching was seen on the NR\_a.c., where  $\Delta H$  is comparable to the deproteinized the dNR\_KOH sample. The effect is related to the removal of natural rubber proteins by water, as most of the stabilizer is believed to migrate to the rubber surface soon after the film formation. The effect of leaching on  $\Delta H$  of the NR\_KOH is lower than on the NR\_a.c., which may be related to the effect of KOH on proteins, or the contribution of the





**FIGURE 12** The main property comparison of the samples stabilized with (a) ammonium caseinate; and (b) KOH (Properties improve from the center of the spider-chart having the worst value in the center) [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

ammonium caseinate stabilizer residuals. Treatment with acetone allowed hysteresis reduction, but it was not as pronounced, as in the case of leaching. Therefore, leaching is preferred method of reducing  $\Delta H$  in latex rubber films.

When latex is stretched and left at that elongation, rubber molecules start rearranging and slipping along one another, which results in the reduction of stress required to maintain this strain level. As the stress relaxation is a major drawback for some of the materials used in DEG, the effect of proteins, stabilizers and post-treatment needed to be evaluated. According to the data presented in Table 7, all the compounds have pronounced stress relaxation, and leaching of the samples seems to have little effect on the stress loss at 1 min. However, leaching led to small reduction in stress loss of the NR\_a.c. samples at 5 and 60 min. The positive effect of acetone-treatment on loss reduction can be related to the removal of “weak” uncrosslinked chains that would otherwise contribute to the stress relaxation by slippage. Among the different rubbers, deproteinized dNR had clearly the lowest stress relaxation. Stress loss of the dNR\_KOH was a little higher than of dNR\_a.c., which may be related to the effect of KOH stabilizer on proteins, which reduces the rubber-protein bond strength and allows more stress to be lost during the stretch.

In order to visualize the effect of the stabilizer and NR type on the combination of studied properties, the spider-charts were used (Figure 12). The chart indicates that NR samples showed better overall properties when ammonium caseinate stabilizer was used, while dNR samples were similar to one another. When only KOH-stabilized samples were considered, both methods of posttreatment were found to give the best combination of properties. As the efficiency of the DEG is very much

dependent on the type of the generator and electrodes, applied bias voltage, prestretch, operation frequency, and so forth (the efficiency of the devices can vary from 2 to 37%<sup>[41,42]</sup>), the properties of the films are compared with the commercial acrylic tape VHB 4905 by 3 M, which is used in the most DEG prototypes discussed in the literature. According to the measured loss properties (Table S1), the obtained films offered significant reduction of the mechanical losses but showed generally higher dielectric losses at 1 Hz frequency.

## 4 | CONCLUSIONS

Dielectric loss properties are dependent on the time after sample curing, when the testing is performed at the same temperature and humidity conditions. The change in dielectric properties with time is believed to depend on many factors with overlapping effects. In natural rubber compounds, the differences can be originating mostly from the migration of the stabilizers and water-soluble proteins to the surface of the sample. According to the data obtained in the present study, the dielectric testing of rubber samples is recommended to be performed between 2 and 4 weeks after sample vulcanization. Among the natural rubber samples, deproteinized latex films show generally lower dielectric losses in 0.1–10 Hz range compared to the standard NR, and less time-dependency of the dielectric losses. The effect can be related to the reduced protein content in such films. In terms of mechanical energy dissipation, deproteinized compounds show lower hysteresis loss and stress relaxation without changing the modulus of the material.

The addition of different stabilizers is found to cause differences in the dielectric losses of the rubber films,



which can be related to the way the additives affect the proteins, including insoluble proteins in the rubber membrane. Ammonium caseinate stabilizer provides lower dielectric losses in 0.1–10 Hz range. However, when the curing time of the samples is changed and a denser crosslink network is created, the use of KOH as a stabilizer is preferred. This may be related to the restricted protein mobility at higher crosslink density. For the deproteinized natural rubber samples, the ammonium caseinate stabilizer is preferable due to the lower hysteresis and stress relaxation.

Among the posttreatment methods, leaching in water helps to decrease the dielectric losses of all natural rubber films more than the acetone-treatment. Both leaching and acetone treatment show reduction in mechanical losses of the samples. As leaching is already applied in latex industry and does not involve the use of chemicals, this method is preferred over the acetone-treatment for the reduction of material-related losses of natural rubber films. Therefore, due to low dielectric and mechanical energy dissipation, leached deproteinized natural rubber stabilized with ammonium caseinate is believed to have high potential in DEG application.

## ACKNOWLEDGMENTS

The study is supported by the Tampere University Graduate School and by the Finnish Foundation for Technology Promotion (TES) grant. The Elastomer Technology and Engineering chair at the University of Twente, Netherlands is acknowledged for the use of the tensile testing equipment. Centrotech Deutschland GmbH is acknowledged for providing the latexes for the study.

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## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

**How to cite this article:** Shakun A, Sarlin E, Vuorinen J. Energy dissipation in natural rubber latex films: The effect of stabilizers, leaching and acetone-treatment. *J Appl Polym Sci.* 2020;e49609. <https://doi.org/10.1002/app.49609>