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TESTING

## Material Properties

## Influence of crosslinker and water on cyclic properties of carboxylated nitrile butadiene rubber (XNBR)

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## ABSTRACT

This study evaluates the effect of network structure (ionic versus covalent crosslinks) on the mechanical behavior of carboxylated nitrile butadiene rubber (XNBR) under cyclic loading. Additionally, the influence of water on the mechanical properties of the XNBR networks is assessed. Reversible and dissipated energies of cyclic tests (with constant maximum strain in each cycle) and step cycle tests (with increasing maximum strain in each cycle) of non-swollen and swollen samples are determined as a function of the used crosslinking system. Energies obtained from step cycle tests are compared to total absorbed energies obtained from monotonic tensile tests. The results show a good correlation between network structure and cyclic behavior. Ionic rearrangement processes are found to be more pronounced in samples with higher ionic crosslinker content. The introduction of covalent crosslinks imparts spatial restriction to ionic rearrangement and improves the cyclic performance of XNBR films upon water exposure.

## 1. Introduction

The introduction of ionized (or ionizable) groups into rubbers allows for tailoring the physical and mechanical properties in a wide range. So-called ionomers exhibit thermoplastic behavior and re-healing properties upon temperature increase [1–3]. One example of an ionomer is carboxylated nitrile butadiene rubber (XNBR), which possesses ionizable carboxylic acid groups in addition to acrylonitrile units and carbon-carbon double bonds. Due to its high polarity, it is typically used in oil-resistant applications such as seals and hoses, or it is applied as memory shape material. In latex form, typical applications include gloves, binders and coatings [4–8]. The acrylonitrile content directly correlates with the glass transition temperature and polarity of the rubber and thus allows for the tuning of physical and mechanical properties. Along with the co-monomer content and the molecular weight distribution of the rubber, the final material behavior is also governed by the network structure, i.e. type and number of crosslinks [7].

The structure of XNBR enables the formation of both covalent and ionic crosslinks. In particular, covalent crosslinks are generated across the carbon-carbon double bonds of the butadiene units in a thermal

curing process by using peroxides or sulfur (in combination with accelerators), or by photo-polymerization with multifunctional thiols as crosslinker. Furthermore, covalent links can be introduced across the carboxylic acid groups by using polyamine salts, polyisocyanates, polyepoxides or polyols [9,10]. Regarding the formation of ionic bonds, typical curing agents are ZnO and MgO, which not only form divalent crosslinks between two carboxylate groups but also aggregate to so-called multiplets (or clusters) consisting of several ion-counterion units. These ionic clusters are large crosslinks and reach diameters of up to 10 nm [11–16]. It was shown that not only divalent but also monovalent ions undergo cluster formation and can therefore be used as crosslinker [16]. Clusters are able to undergo ionic rearrangement processes and thus significantly influence material properties [1–3].

In preceding work, the effect of network structure on the static performance of XNBR was investigated [17]. In engineering applications, failure of rubber goods usually does not occur within one single loading but rather results from crack growth under cyclic loading [18]. Thus, in this study, focus was put on the effect of network structure on the cyclic behavior of XNBR. Elastically stored and dissipated energies of XNBR samples were determined in dependence on the network structure and compared with corresponding energies obtained from

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monotonic tensile tests (which can be seen as single-cycle tests). Elastomers exhibit a characteristic stress-softening effect upon cyclic loading, which has been first investigated in detail by Holt for filled elastomers in the 1930s [19] and was analyzed thoroughly by Mullins in the 1940s [20,21]. Harwood [22] found in the 1960s that both unfilled and filled elastomers exhibit such a hysteretic behavior. This characteristic behavior of elastomers is of high importance for material properties such as abrasion, tear resistance and heat build-up. It is caused by several mechanisms involving (i) breakage of filler agglomerates, (ii) bond rupture (intensified by the addition of filler, which causes local stress concentrations), (iii) orientation of polymer chains upon stretching followed by closer package and/or crystallization, (iv) internal friction, (v) molecule slipping, disentanglements, network rearrangements (irreversible processes) as well as (vi) viscoelastic behavior of elastomers (time-dependent deformation) [18,20–26].

The exposure of elastomers to liquids causes enormous changes in the network structure and material behavior due to the diffusion of molecules of the liquid into the elastomeric bulk, which leads to swelling and forces the polymer chains apart [17,27–29]. The investigation of the hysteretic nature of swollen elastomers and hydrogels is described in several articles. Webber et al. performed cyclic tests on double-network hydrogels which showed a large hysteresis loop during the first cycle followed by smaller loops in subsequent cycles. This effect was attributed to the existence of dissipative processes and was published for the first time in polymer gels [30]. Another study focused on cyclic testing of silica hydrogel hybrids [31]. Chai et al. [32–34] developed a compression device to subject swollen elastomers to cyclic testing. The investigation of the swelling behavior of nitrile butadiene rubber (NBR) and polychloroprene rubber (CR) in biodiesel revealed a reduction of the strength of elastomers upon swelling. In further investigations [35], a model was developed to describe the Mullins effect of swollen elastomers and experimentally tested with NBR, showing a good agreement of the proposed model with experimental results. Cantournet et al. designed a 3D model to display dissipative processes that occur during cyclic testing, which was experimentally proven by testing natural rubber (NR) and styrene butadiene rubber (SBR) [23]. As the use of XNBR as glove material, binder or coating requires resistance to water [36–38], the effect of water exposure on the cyclic performance of XNBR comprising different crosslinker was assessed. The results show a strong dependence of the cyclic properties of XNBR films on network structure and water exposure, thus evidencing the importance of network design on the material performance of final products.

## 2. Experimental

### 2.1. Materials and chemicals

XNBR latex (Nipol LX556) with a pH value of 8.5, an acrylonitrile content of 31% and a dry rubber content of 45 wt.-% was supplied by ZEON (Japan). Aqueous sulfur and zinc oxide dispersions were provided by Semperit Technische Produkte (Austria). The photoinitiator ethyl-2,4,6-trimethyl-benzoyl-phenylphosphinate (Irgacure TPO-L) was obtained from BASF (Germany), the trifunctional thiol trimethylolpropane tris-3-mercaptopropionate (TMPMP) was purchased from Bruno Bock Thiochemicals (Germany) and the antioxidant Ralox LC was supplied by Solvadis (Germany). The emulsifier Tween<sup>®</sup>20 and potassium hydroxide ( $\geq 85\%$ ) were purchased from Sigma Aldrich (US). All chemicals were used without further purification. The compositions of the XNBR samples that were used in this work are given in Table 1.

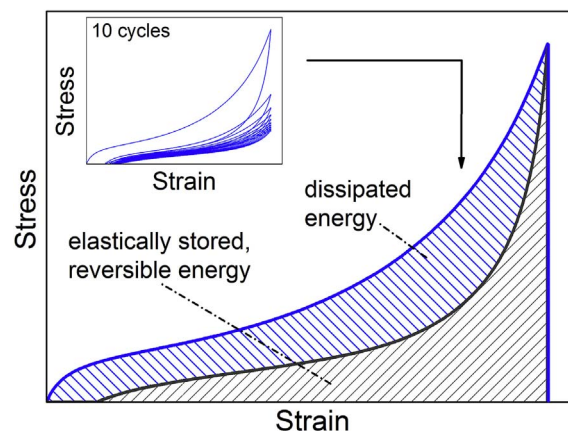
### 2.2. Preparation of cured XNBR films

#### 2.2.1. Thermal pre-curing of XNBR latex

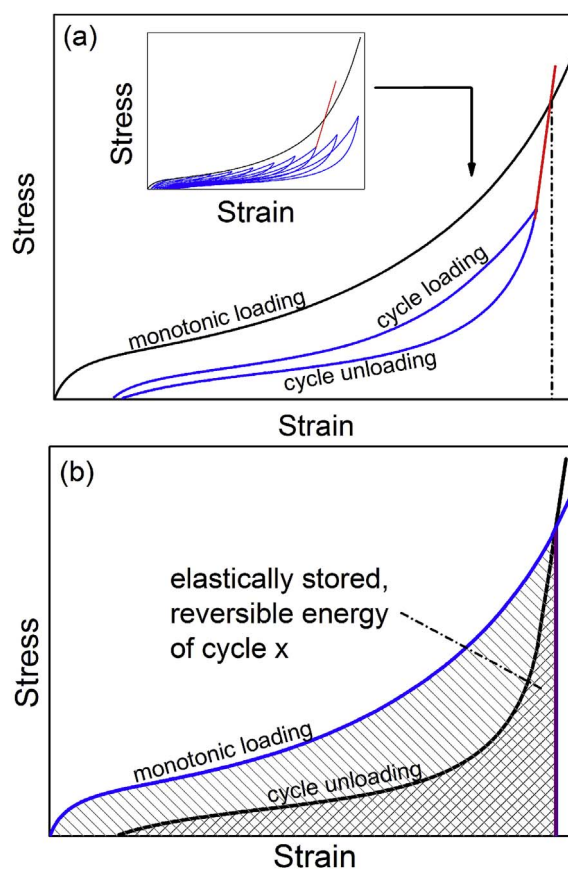
The pH value of the XNBR latex was adjusted to 10.2 by adding a KOH solution (1 wt.-%) under stirring. For the ionic crosslinking, 0.5

**Table 1**  
Composition of XNBR samples.

Sample name	XNBR (phr)	KOH (phr)	ZnO (phr)	TMPMP (phr)	Sulfur (phr)
XNBR-KOH	100	1.8	–	–	–
XNBR-0.5ZnO	100	1.8	0.5	–	–
XNBR-ZnO-S	100	1.8	0.5	–	1
XNBR-ZnO-thiol	100	1.8	0.5	1	–
XNBR-2ZnO	100	1.8	2	–	–



**Fig. 1.** Cyclic loading to a constant strain for ten times (inset); illustration of energy components of one hysteresis (the sum of dissipated and elastically stored energy is the total absorbed energy).



**Fig. 2.** Comparison between stress-strain curve (monotonic loading) and step cycle tests; (a) the unloading curve obtained by step cycle testing is linearly interpolated up to the point of intersection with the stress-strain curve; (b) energy components.

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