Exploring various metal-ligand coordination bond formation in elastomers: Mechanical performance and self-healing behavior

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Abstract. Dynamic covalent crosslinking such as disulfide bonds, Diels-Alder (DA) reactions are widely used for healing applications. Herein, we report a simple approach involving the metal-ligand reversible interactions in diverse nature, which helps in developing a robust and self-healable carboxylated nitrile (XNBR) rubber by employing low cost and the commercially obtainable materials. Self-healing performance and mechanical properties were organized by introducing the various metal-ligand domains into the XNBR rubber. The network of XNBR, in-situ cross-linked via metal-ligand complexes, consists of strong and weak coordination bonds. The strength of various metal-ligand modified coordination bonds, healing performance, and mechanical properties primarily depend on the type of metal ions. The Fourier transform infrared spectroscopy (FTIR) makes the various metal-ligand coordination bond formation into the XNBR rubber visible. The coordination crosslinked XNBR rubber with 4 phr of Zn and Co metal ion exhibits high tensile strength (4.3 ± 0.6 and 10.3 ± 1.1 MPa) with excellent healing efficiency (100 and 88%), which is far higher than the most reported non-covalent supramolecular modified elastomers. The various metal-ligand coordination bonds are fully reconstructed during the rebuilding process and exhibiting excellent self-healing property.

Keywords: mechanical properties, XNBR rubber, various metal-ligand bond, self-healing

1. Introduction

Rubber is a virtually incompressible material that exhibits high elasticity; its phenomenal flexibility is often explored in various applications such as, hoses, seals, tires, shock absorbers, etc. Natural rubber (NR), polybutadiene rubber (BR), ethylene-propylene-diene rubber (EPDM), acrylonitrile-butadiene rubber (NBR), and styrene-butadiene (SBR) are some common examples of a widely used elastomer in day to day life [1]. In the recent developments over the past few decades, the idea of commercially adaptable characteristics that enable spontaneous healing or mending of damages in the rubbery product has gained tremendous popularity [2, 3]. Rubbers with such attributes are popularly known as self-healing rubbers

[3, 4]. Self-healing rubbers exhibit built-in ability to repair damage to themselves spontaneously. Such additional value to the rubbery materials is beneficial, especially taking into account that rubbers are prone to fatigue and environmental conditions. The self-healing characteristics enhance the longevity of rubber-based products [5].

Elastomers that possess self-healing ability can be broadly divided into two classes, *i.e.*, autonomous [6–8] and non-autonomous self-healing rubbers [9]. The autonomous self-healing polymers follow a process very similar to that of a biological response [9], which does not require external intervention [10]. Polymers with a kind of encapsulated internal adhesives were the first synthetic materials to be reported

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as autonomous self-healing material in 2001 by White [6], Nancy Sottos, and colleagues from the University of Illinois [6]. After that, many other self-healing materials [11] were developed. On the other hand, the non-autonomous self-healing rubbers [12] require some form of external stimuli such as heat, light, mechanical, or chemical. Terryn *et al.* [13] and Habault *et al.* [14], have proposed the heat stimulated self-healing elastomers [13]. Moniruzzaman *et al.* [16] and Amamoto *et al.* [17] have suggested light-induced self-healing rubbers, and Rekondo *et al.* [20] have worked on the mechanochemical self-healing elastomers [14, 15]. Some specific interactions through noncovalent bonding such as hydrogen bonding [16], metal-ligand coordination [17–20], host-guest interactions [21, 22], ionic bonds [23–25], van der Waals forces, π - π interactions, halogen bonding [16, 26], etc., and some dynamic covalent bonds like Diels-Alder [27–29], disulfide bonds [30], imine bonds, etc., are involved in the majority of the strategies for the development of self-healing elastomer. These specific interactions are collectively known by the term ‘molecular recognition’ [31, 32].

Experiments involving the concept of self-healing have been reported, but very few have worked on the challenges and limitations of developing the self-healing elastomer [12] that possesses good healing efficiency and good mechanical strength. Inspired by Wang *et al.* [4], and Cheng *et al.* [33] it has been

reported that the recyclability of dopamine grafted epoxidized nitrile rubber with 2.5 phr of ferric chloride reached 8.93 MPa tensile strength. We report a simple preparation and testing a design for the structural rubbery materials that exhibit excellent robustness and good self-heal efficiency [34]. This study compares the effect of different types of metal-ligand coordination systems [35–37], introduced via general-purpose rubber equipment, on the mechanical properties and self-healing behavior of the rubbery material. Our self-healing experiments yield as much as 88% recovery of 10.3 MPa tensile strength. We expect our approach (Figure 1) to apply to a wide variety of rubbers.

2. Experimental sections

2.1. Materials

Carboxylated nitrile-butadiene rubber (XNBR, Krynac® X 750, by Lanxess, Germany), consisting of 7 wt% carboxylic group and 27 wt% acrylonitrile content, was directly used. Specific gravity and Mooney viscosity (ML 1+4 @ 100 °C) of the rubber was found to be 0.99 and 47 respectively. The metal salts, cobalt(II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Co^{2+} , 98%); nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Ni^{2+} , 98%); zinc(II) nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Zn^{2+} , 98%), were purchased from Sigma-Aldrich. The ligand, 2,6-diaminopyridine (DAP, 98%) was purchased from Sigma-Aldrich; all reagents were analytical grade and used as received.

Figure 1. The proposed model of the multiple metal-ligand bonds in XNBR. The solid line indicates the strong metal-ligand bond and the dashed line indicates the weak metal-ligand bond.

2.2. Preparation of XNBR-DAP-metal ion complexes

2,6-diaminopyridine, cobalt(II) nitrate hexahydrate, nickel(II) nitrate hexahydrate, and zinc(II) nitrate hexahydrate were mixed with carboxylated nitrile rubber (XNBR) in two successive steps, according to the compounding formulation (Table 1). First, XNBR and DAP (1:1-mole ratio COOH group in XNBR: DAP ligand, which was converted into phr) were mixed inside the chamber of an internal mixer (Thermo Haake Poly Lab oS Rheo Drive4) for 30 min, at 130 °C and 60 rpm rotor speed. Then the DAP-XNBR compound was homogenized by a two-roll mixing mill (Polymix 110L, size 203×102 mm, Servitech GmbH, Wustermark, Germany) for 2 min. The amide linkage was brought about by DAP-carboxyl chemical reactions into the XNBR rubber, during this first step (as revealed by FT-IR analysis).

In the second step, different rubber compounds were prepared by mixing various metal salts with the aforementioned modified XNBR rubber. The ingredients were mixed inside the chamber of an internal mixer at 100 °C for 10 min with a rotor speed of 60 rpm. After mixing, the rubber compounds were homogenized by a laboratory size two-roll mixing mill for 2 min. Then, rubber compounds were compression molded at 170 °C [33] and 5 MPa pressure for 30 min by using a hydraulic press (Moore Hydraulic Press, England), and the molded specimens were cooled under pressure to protect the total dimensional stability. The final molded samples were subjected to various analyses, such as FT-IR spectroscopy, stress-strain, etc., to understand the effect of incorporation of metal salts towards the properties improvement and self-healing ability.

2.3. Characterization

2.3.1. Fourier transform infrared (FTIR) spectroscopy

The FTIR analysis was accomplished to find out the interactions in the rubber compounds. The spectra of

Figure 2. FTIR spectra of pristine XNBR, neat DAP ligand, and XNBR+DAP compound.

samples were obtained by using the Perkin Elmer spectrometer, over the wavenumber 500 to 4000 cm^{-1} range, and an attenuated total reflectance (ATR) mode setup. The number of scans for each sample was 8. The FTIR spectra of XNBR, DAP ligand, and XNBR+DAP compounds were shown in Figure 2. In the case of pristine XNBR, the characteristic peaks at 2919 and 2844 cm^{-1} (not indicated in figure) correspond to the stretching vibrations of CH_2 groups [38], the peak at 2234 cm^{-1} was ascribed to the $-\text{CN}$ groups of the acrylonitrile moiety of XNBR [38], Peaks at 1725 and 1694 cm^{-1} correspond to the $-\text{COOH}$ groups of the acrylic acid moiety of XNBR and $-\text{C}=\text{O}$ stretching vibration of carboxylic groups, respectively. Whereas, neat DAP ligand [39, 40], peaks at 3425, 3251, 3206, 1637, and 1580 cm^{-1} were attributed to the $-\text{NH}$ asymmetric stretching, $-\text{NH}$ symmetric stretching, $\text{N}+\text{H}$ stretching vibrations, $-\text{NH}$ bending vibrations of NH_2 groups, and the $\text{C}=\text{C}$ stretching vibrations of free pyridine, respectively. After introducing the DAP ligand into XNBR rubber, a newly characteristic absorption peak at 1693 cm^{-1} (amide band [4] I) and 1618 cm^{-1} (amide band [4] II) (indicated in Figure 1) are due to the amide formation ($-\text{CO}-\text{NH}-$) between the $-\text{COOH}$

Table 1. Formulations of all the rubber compounds.

Sample name	Ingredients [phr]				
	XNBR	DAP	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
XNBR+DAP	100	12	—	—	—
XNBR+DAP+ Co^{2+}	100	12	4	—	—
XNBR+DAP+ Ni^{2+}	100	12	—	4	—
XNBR+DAP+ Zn^{2+}	100	12	—	—	4

group of XNBR and the NH_2 of DAP ligand. The peak at 1453 cm^{-1} is observed of DAP ligand, which is the $\text{C}=\text{N}$ vibration modes of free pyridine and the exhibits at 1301 cm^{-1} is the $\text{C}-\text{N}$ stretching vibrations of free pyridine and the peaks at 3457 , 3304 and 3216 cm^{-1} attributes to the $-\text{NH}$ asymmetric, symmetric and N^+-H stretching vibrations of the DAP ligand.

2.3.2. Mechanical properties

The tensile experiment of all samples was performed using a Universal Testing Machine (Hounsfield H25KS) apparatus, according to the ASTM D-412 standard. An extension rate of 500 mm/min and room temperature conditions were used for the experiment. A dumbbell-shaped sample specimen, 20 mm gauge length and 3 mm width in dimension, was placed in the grips of the testing machine.

2.3.3. Self-healing properties

The self-healing experiment of all samples was performed using a Universal Testing Machine (UTM). The standard dumbbell-shaped samples were cut from the middle using a scissor into two separate pieces; the freshly cut surface of samples was held together inside a vacuum oven for various length of time (0.5 , 1 , 3 , 6 , 12 , and 24 h). The healing efficiency of various samples was also studied at different temperatures (RT , 40 , 60 and 80°C). The self-healing efficiency [34] (η) is defined as the ratio of the tensile strength of the healed sample (σ_{healed}) to the virgin sample (σ_{pristine}), Equation (1):

$$\eta = \frac{\sigma_{\text{healed}}}{\sigma_{\text{pristine}}} \cdot 100 \quad (1)$$

The healing process of metal-ligand crosslinked elastomer was shown in Figure 3.

2.3.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry studies were performed using the DSC 204F1, NETZSCH (Germany) instrument. About 8 to 10 mg of sample was weighed and placed inside the DSC aluminum pan, and in the temperature range of -100°C to room temperature, at the heating rate was 10°C/min under the liquid nitrogen atmosphere.

2.3.5. Scanning electron microscopy (SEM)

The morphologies of all samples were examined using a Field Emission Scanning Electron 348 Merlin Microscope (Germany). All the samples were cryo-fractured using the liquid nitrogen, and then the fractured surfaces were probed. Prior to the SEM test, the surface of all samples was sputtered with gold to provide improved conductivity.

2.3.6. Atomic force microscopy (AFM)

The depth profilometry of cut and healed surfaces were compared using AC-AFM Agilent 5500 Scanning Probe Microscope (USA) under tapping mode. The cantilever frequency was 150 kHz , and the force constant was 42 N/m .

2.3.7. Optical microscopy

The optical microscope (ZEISS Scope.A1 AX10) was deployed for surface damage-control analysis through the course of the healing process.

Figure 3. The healing process of the multiple metal-ligand crosslinked elastomers.

2.3.8. Rubber process analyzer (RPA 2000)

Stress relaxation analysis of all samples was carried out using the rubber process analyzer (RPA 2000, Alpha Technologies, USA). Approximately 5 g of sample was subjected to a 3° angular strain, while the temperature of upper and lower platens was maintained at 170 °C temperature. The decay in the modulus was monitored over a period of 12 min.

2.3.9. Tension set

The tension set experiment of all samples was performed using a Universal Testing Machine (Hounsfield H25KS) apparatus, and the dumbbell specimens were enlarged (stress at 100% MPa) in the tensile direction at an extension rate of 50 mm/min and keep at that position for 10 minutes at room temperature. It was then relaxed back to unstressed condition, and the percentage change in dimension in tensile direction was measured after 20 minutes and reported as tension set (Equation (2)):

$$\text{Tension set [\%]} = \frac{\text{Change in length}}{\text{Original length}} \cdot 100 \quad (2)$$

2.3.10. Swelling experiments

The swelling experiment of all the rubber compounds was studied using a toluene solvent (molar volume 107 cm³/g). The sample was cut into a round size and then swollen in a toluene (reagent grade purity) solvent with the idea of the polymer-solvent interaction parameter. Preweighted rubber samples are swollen for 72 h at room temperature. After swelling (72 h), the solvent is dry quickly from the surface of the rubber specimen by a clean tissue paper, and then final weights were taken. The cross-link density, v_e [cm⁻³] was got by using Equation (3):

$$v_e = \frac{\rho_p N_A}{M_c} \quad (3)$$

where ρ_p is the polymer density, N_A is the Avogadro's number, and M_c is the average molecular weight of the chain during cross-links. In a swelling study, the Flory equation (Equation (4)) is widely used to determine the M_c value:

$$M_c = -V_s \rho_p \frac{\phi_p^{1/3} - 0.5\phi_p}{\ln(1 - \phi_p) + \phi_p + \chi\phi_p^2} \quad (4)$$

where M_c is the average molecular weight of the polymer chain between cross-links, V_s is the solvent

molar volume, ϕ_p is the polymer volume fraction in the swollen specimen, and χ is the polymer-solvent interaction parameter [38]. The value of χ is taken as 0.34.

2.3.11. Moving die rheometer (MDR) study

The rheometric characteristics of all the samples were studied using moving die rheometer (MDR), Monsanto MDR-2000 (USA) at temperature 170 °C for 30 min. The experiments were carried out at 70 psi die pressure, 1.7 Hz (100 CPM) frequency, and an oscillatory rotation amplitude of 0.5° arc.

2.3.12. High-resolution transmission electron microscope (HR-TEM) study

The morphologies of all the rubber compounds were examined using a JEM-2100 HR-TEM, Make-JEOL, Japan, point to point resolution (0.194 nm) and 200 kV electron beam accelerating voltage. The samples were prepared using the ultramicrotome cutting instrument.

3. Results and discussion

3.1. Incorporation of DAP ligand and metal ion into XNBR

The successful formation of amide linkage between the -COOH group of XNBR and the -NH₂ group of DAP ligand and formation of coordination complexes of DAP ligand with various metal ions was confirmed by FTIR analysis. The FTIR spectra of XNBR, DAP ligand, DAP modified XNBR compound was discussed in Section 2.3.1 and various coordination cross-linked rubber samples (with Co²⁺, Ni²⁺, and Zn²⁺) were shown in Figure 4. After introducing various metal salts into the DAP modified rubber, several characteristic peaks were observed that confirm the successful formation of the coordination complex. Upon complexation with Co²⁺, the peak ascribed to C=N bending vibration of DAP ligand shifted from 1453 to 1438 cm⁻¹ and the C-N stretching vibration of ligand shifted from 1301 to 1339 cm⁻¹, because of the coordination bonding between pyridine part of the DAP ligand and Co²⁺ metal ion. The peaks at 1693 cm⁻¹ (amide band I) and 1618 cm⁻¹ (amide band II) of amide linkage DAP shifted to 1678 and 1655 cm⁻¹ after complexation with Co²⁺ metal ion, indicating the complexation of Co²⁺ ion through oxygen and nitrogen atoms of the amide group, and also the -NH asymmetric,

Figure 4. FTIR spectra of various metal-ligand modified rubber compounds.

symmetric and N-H stretching vibrations were observed, similar developments were observed the case of Ni and Zn salt-based rubber composites; the C=N vibrations peak at 1453 cm^{-1} is shifted to 1438 cm^{-1} and the C-N stretching vibration of ligand shifted from 1301 to 1339 cm^{-1} upon complexation with Ni^{2+} and Zn^{2+} metal ions. The amide band I and amide band II are shifted from 1693 and 1618 cm^{-1} to 1678 and 1655 cm^{-1} , respectively after complexation with metal ions. The FT-IR results were strong evidence that the formation of amide linkage between COOH groups of XNBR rubber and the NH_2 groups of DAP ligand (Figure 2), after addition of various metal ions on XNBR+DAP system, metal-ligand coordination bond was formed (Figure 4). This metal-ligand coordination bond was dynamic and reversible in nature because after cut the sample, the coordination bond broke down and then reformed at a certain temperature and time (Figure 9).

3.2. Mechanical properties of metal-ligand modified rubber composites

The mechanical properties of various rubber compounds are summarized in Table 2. The XNBR-DAP- Co^{2+} compound was shown the highest tensile strength up to 10.3 MPa compared to Ni and Zn salt

compounds, due to sufficient metal-ligand cross-linked into rubber network and electronic configuration of the metal ion. XNBR+DAP sample was exhibited the highest elongation at break, highest tension set, and lowest tensile strength due to the absence of metal ions that do not form any crosslinking network with the DAP ligand. The tensile strength of the uncured XNBR sample is around 0.5 MPa .

Mechanical properties of XNBR with various metal ions modified rubber composites

We have studied the mechanical properties of XNBR rubber with various metal-ligand modified compounds, and the XNBR rubber with only various metal ions compound are summarized in Table 2 and Table 3. The result shows that the mechanical properties depend on the types of metal ions used in the system.

3.3. Differential scanning calorimetric (DSC) study

A differential scanning calorimetry study to finding the glass transition temperature of the metal-ligand cross-linked samples is shown in Figure 5 and the data in Table 4. The DSC glass transition temperature of virgin XNBR is -25.2°C and, after treatment with DAP ligand is a shift to the -23.3°C and then after treatment with the various metal ions, the glass transition temperature is increased, because of the metal ion is cross-linked with the DAP ligand into the XNBR chain. The XNBR-DAP/ Co^{2+} sample, the glass transition temperature is -15.6°C , XNBR-DAP/ Ni^{2+} sample is -14.7°C and, the XNBR-DAP/ Zn^{2+} sample is -18.6°C due to the Ni-DAP bond is

Table 3. The mechanical properties of XNBR with various metal ions modified rubber compounds.

Sample name	T.S [MPa]	EB [%]	300% modulus [MPa]	Hardness [Shore A]
XNBR+ Co^{2+}	8.4 ± 0.8	1456	1.5	54 ± 2
XNBR+ Ni^{2+}	6.8 ± 0.5	1344	1.8	55 ± 2
XNBR+ Zn^{2+}	3.7 ± 0.4	1005	1.2	48 ± 2

Table 2. The mechanical properties of various rubber compounds.

Sample name	T.S [MPa]	EB [%]	300% modulus [MPa]	Hardness [Shore A]	Tension set [%]
XNBR+DAP	0.7	>2000	0.3	40 ± 1	70 ± 2
XNBR+DAP+ Co^{2+}	10.3 ± 1.1	1436	2.1	60 ± 2	33 ± 2
XNBR+DAP+ Ni^{2+}	8.6 ± 0.9	1450	1.6	59 ± 1	17 ± 2
XNBR+DAP+ Zn^{2+}	4.3 ± 0.6	1560	0.8	52 ± 1	45 ± 2

Figure 5. The differential scanning calorimetry (DSC) study of pristine XNBR, XNBR+DAP, XNBR-DAP/Co²⁺, XNBR-DAP/Ni²⁺, and the XNBR-DAP/Zn²⁺ samples.

stronger than the Co-DAP bond and the Zn-DAP bond, the Zn-DAP bond is more dynamic as compared to the Co and Ni metal ions.

Because of the electronic configuration of metal ions, in the case of Zn metal ion, the electronic configuration is $3d^{10}4s^2$, d -orbitals are completely fillup, so ligands are not able to attach with the non-bonded electron of d -orbitals. In this case, the ligands are loosely attached to an outer shell of the metal ions. Whereas Co and Ni the electronic configurations are $3d^7$ and $3d^8$, so ligands are able to attach with the non-bonded electron of d -orbitals, that's why Zn-DAP bonds are more dynamic in nature as compared to Co-DAP and Ni-DAP bonds. So, in the case of XNBR-DAP/Ni²⁺ sample, the metal-ligand cross-linked density is higher, and the glass transition temperature is also higher as compared to the XNBR-DAP/Co²⁺ and the XNBR-DAP/Zn²⁺ sample.

3.4. Rubber process analyzer (RPA 2000).

Stress-relaxation analysis was carried out at typical rubber processing temperature, *i.e.*, 170 °C by using

Table 4. The glass transition temperature (T_g) of various rubber compounds.

Sample name	Glass transition temperature, T_g [°C]
XNBR	-25.2
XNBR+DAP	-23.3
XNBR+DAP+Co ²⁺	-15.6
XNBR+DAP+Ni ²⁺	-14.7
XNBR+DAP+Zn ²⁺	-18.6

Figure 6. The stress-relaxation study of the XNBR+DAP, XNBR+DAP+Co²⁺, XNBR+DAP+Ni²⁺, and XNBR+DAP+Zn²⁺ samples.

the rubber process analyzer, which is shown in Figure 6, and the data in Table 5. According to the Maxwell model (Equation (5)), where σ_0 is the original stress required to bring about the deformation and the σ is the stress at a time t after the material stays under the constant deformation and the t_{rel} ($= \eta/G$) is the relaxation time, η and G are the viscosity and the modulus of the materials. The t_{rel} indicates the time taken for the stress to fall to a value $1/e$ times, which is $1/2.7 = 0.367$ or 0.37 times σ_0 . The relaxation time of XNBR+DAP+Ni²⁺ sample is higher than XNBR+DAP+Co²⁺, and XNBR+DAP+Zn²⁺ samples, which suggest higher metal-ligand cross-linked network formation and the Ni-DAP bond is not so dynamic in nature, which results in the lower self-healing performance. But the XNBR+DAP+Co²⁺ sample, the relaxation time is quite higher than the XNBR+DAP+Zn²⁺ sample, in both cases, the Co-DAP bonds and the Zn-DAP bonds are dynamic in nature and the advantage to the higher heat-induced self-healing ability.

The Zn-DAP bonds are formed a weak coordination bond (shown in Figure 1) due to the electronic configuration of Zn metal ion ($3d^{10}4s^2$) and, as discussed in detail Section 3.3. The relaxation time of XNBR+DAP sample is very lower, because in the absence of metal ions, having no crosslinking site, so do not exhibit self-healing behavior.

The stress relaxation in RPA and the glass transition temperature in DSC study are clear evidence that the XNBR+DAP+Ni²⁺ specimen has the highest relaxation time and highest glass transition temperature due to the highest metal-ligand crosslinked density

Table 5. The normalized relaxation modulus corresponding with the relaxation time of the metal-ligand modified XNBR elastomer.

Sample name	Normalized relaxation modulus	Relaxation time [s]
XNBR+DAP	0.367	0.043
XNBR+DAP+Co ²⁺	0.367	0.084
XNBR+DAP+Ni ²⁺	0.367	0.128
XNBR+DAP+Zn ²⁺	0.367	0.048

and strong metal-ligand coordination bond formation than the Co and Zn samples.

The room temperature tensile strength of XNBR+DAP+Zn²⁺ (Table 2) compound is much higher than the XNBR+DAP (without metal ion) sample but relaxation time (Equation (5)) at 170 °C of XNBR+DAP+Zn²⁺ is quite higher than the XNBR+DAP compound due to polymer/ligand or ligand/ metal ion reaction occurred at elevated temperature:

$$\sigma = \sigma_0 \cdot e^{-\frac{t}{t_{rel}}} \quad (5)$$

3.5. Self-healing and mechanical properties of the multiple metal-ligand modified XNBR

3.5.1. The effect of temperature on healing performance and mechanical properties

The carboxylated nitrile rubber (XNBR) was cross-linked by coordination complexes of various metal salt and DAP ligand. The corresponding elastomers (XNBR-DAP/Co²⁺, XNBR-DAP/Ni²⁺, and XNBR-DAP/Zn²⁺) were obtained after the compression molding. The mechanical properties and healing

performances are tabulated in Table 6. The XNBR-DAP ligand (Reference sample), which is not healed (Figure 15), because of the absence of metal ion, does not form any metal-ligand coordination bond. The mechanical properties of Co-based compounds show higher value with respect to other metal moieties like Ni and Zn metal ions due to the different electronic configurations and complex formation. The electronic configuration of Co metal is 3d⁸4s², *d*-orbital have more vacant site (free electron), the ligand can easily attach with metal ion and formed a stable coordination complex. Whereas Ni metal ion, the electronic configuration is 3d⁸4s², *d*-orbital has the less vacant site (free electron), the ligand can attach with the free electron of *d*-orbital and also an outer shell of this metal ions, can form a strong metal-ligand coordination bond. In the case of Zn metal ion, an electronic configuration is 3d¹⁰4s², *d*-orbital has no vacant site, so ligand can loosely attach with the outer shell of the metal ion. That's why the Co-based complex showed better mechanical properties compared to Ni and Zn metal ions.

The typical stress-strain plots of (XNBR-DAP/Co²⁺, XNBR-DAP/Ni²⁺, and XNBR-DAP/Zn²⁺) are shown in Figure 7. It is obvious that the self-healing performance and mechanical performance of the healed sample can easily be changed by varying the temperature. The healing efficiency increases with increasing the temperature, as shown in Table 6. The modulus values of the healed sample increases with increasing the temperature due to polymer/ligand and ligand/metal ion interaction occurred at elevated temperature. The higher modulus can be a result of

Table 6. The mechanical and self-healing performance at various temperatures with a fixed time for 24 hrs.

Sample name	Temperature [°C]	Tensile strength [MPa]		300% modulus of a pristine sample [MPa]	300% modulus of a healed sample [MPa]	Self-healing efficiency [%]
		Pristine sample	Healed sample			
XNBR+DAP+Co ²⁺	Room temperature	10.3±1.1	2.2±0.9	2.1	1.8	21
XNBR+DAP+Ni ²⁺		8.6±0.9	1.5±0.5	1.6	1.4	17
XNBR+DAP+Zn ²⁺		4.3±0.6	2.4±0.7	0.8	0.9	55
XNBR+DAP+Co ²⁺	40	10.3±1.1	3.0±1.2	2.1	2.0	29
XNBR+DAP+Ni ²⁺		8.6±0.9	1.9±0.8	1.6	1.4	22
XNBR+DAP+Zn ²⁺		4.3±0.6	2.9±0.8	0.8	1.1	66
XNBR+DAP+Co ²⁺	60	10.3±1.1	4.5±0.6	2.1	1.7	44
XNBR+DAP+Ni ²⁺		8.6±0.9	2.1±1.1	1.6	2.1	24
XNBR+DAP+Zn ²⁺		4.3±0.6	3.5±0.7	0.8	0.9	79
XNBR+DAP+Co ²⁺	80	10.3±1.1	9.1±1.3	2.1	2.4	88
XNBR+DAP+Ni ²⁺		8.6±0.9	4.8±1.1	1.6	2.3	56
XNBR+DAP+Zn ²⁺		4.3±0.6	4.4±1.2	0.8	1.3	100

Figure 7. Typical stress-strain plots of virgin and healed samples at different temperatures; (a) XNBR+DAP+Co²⁺, (b) XNBR+DAP+Ni²⁺, and (c) XNBR+DAP+Zn²⁺.

higher mobility of macromolecules of the healed sample.

The tensile strength of XNBR-DAP/Zn²⁺ is 4.3 ± 0.6 MPa, with a 300% modulus ≈ 0.8 MPa for a virgin sample. The XNBR-DAP/Ni²⁺ sample tensile strength reached 8.6 ± 0.9 MPa with a 300% modulus ≈ 1.6 MPa and XNBR-DAP/Co²⁺ sample is 10.3 ± 1.1 MPa with a 300% modulus ≈ 2.1 MPa. The samples of XNBR-DAP/Co²⁺ and XNBR-DAP/Ni²⁺ are harder than the XNBR-DAP/Zn²⁺ sample because Co²⁺ and Ni²⁺ ions are formed a stronger bond with DAP ligand into the XNBR rubber than the Zn²⁺ ion. After that, the healing concert of all various metal-ligand crosslinked XNBR is established.

The specimens are cut into two pieces, then cut specimens are immediately touched together and lightly pressed to secure the good contact, keep it for 1 min at room temperature and then do self-healing test at various temperatures (room temperature, 40, 60, and 80 °C) for a fixed time 24 hrs in a vacuum oven but not in vacuum condition. In the case of XNBR-DAP/Zn²⁺ sample, the self-healing efficiency increases with increasing the temperature. After 24 h of the room-temperature healing process, the healing efficiency was 55% which increased up to 100% after the mending process carried out at 80 °C temperature. Similarly, the healing efficiency of XNBR-DAP/Co²⁺ and XNBR-DAP/Ni²⁺ samples

increases with increasing the temperature. The healing efficiency of XNBR-DAP/Co²⁺ sample after 24 h of the mending process at room temperature and 80 °C is 21 and 88%, respectively. Co²⁺ ion and DAP ligand form a stronger bond as compared to the Zn²⁺ ion. In the case of XNBR-DAP/Ni²⁺ sample, the healing efficiency after 24 h of the mending process is 17% (at room temperature) and 56% (at 80 °C temperature); this is attributed to a more stronger coordination bond between the Ni²⁺ ion and the DAP ligand as compared to coordination bond that Co²⁺ and Zn²⁺ ions forms with DAP ligand in XNBR rubber. In the case of XNBR-DAP/Zn²⁺ sample, after healing at 24 h, the tensile strength of healed sample is higher (4.4±1.2 MPa) than the pristine sample (4.3±0.6 MPa), which could be explained through the extra metal-ligand coordination bond formation that occurs over time at elevated temperature and also maybe the thermo-oxidative aging of the sample when it is exposed in a vacuum oven at 80 °C for 24 hours.

The Young's modulus and yielding stress (Figure 7) of the healed sample became much higher than the virgin sample because of polymer/ligand or ligand/metal ion reaction occurred at elevated temperatures.

3.5.2. The effect of healing time on mechanical properties and healing performance

The effect of healing time on the mechanical and self-healing performances of XNBR-DAP/Co²⁺, XNBR-DAP/Ni²⁺, and XNBR-DAP/Zn²⁺ samples was examined (Table 7), and the typical stress-strain graphs for various samples were plotted (Figure 8).

The results reveal that the self-healing efficiency of samples gradually improves over time. The flawless (uncut) XNBR-DAP/Zn²⁺ sample exhibits 4.3 MPa tensile strength, whereas the mended XNBR-DAP/Zn²⁺ sample exhibits gradual increment in the tensile strength through 1.6; 2.6; 2.9; 3.2; 3.6; 4.4 MPa over 0.5; 1; 3; 6; 12 and 24 h of healing process, respectively. The tensile strength is 4.4±1.2 MPa and the healing efficiency is 100%, and XNBR-DAP/Co²⁺ sample, the tensile strength, and healing efficiency are 9.1±1.3 MPa and 88%, the XNBR-DAP/Ni²⁺ sample, the tensile strength, and the healing efficiency are 4.8±1.1 MPa and 56%. The 24 hours self-healing time is contemplated to supreme and also energy-saving matter.

The recovery of strength and corresponding healing efficiencies through the mending period is shown in Figure 9. The healing results are proposed that the Ni²⁺-DAP bond is stronger than the Co²⁺-DAP and

Table 7. Summary of mechanical and self-healing properties at different times with a fixed 80 °C temperature.

Sample name	Time [hrs]	Tensile strength [MPa]		300% modulus of a pristine sample [MPa]	300% modulus of a healed sample [MPa]	Self-healing efficiency [%]
		Pristine sample	Healed sample			
XNBR+DAP+Co ²⁺	0.5	10.3±1.1	2.7±0.9	2.1	1.9	26
XNBR+DAP+Ni ²⁺		8.6±0.9	1.5±1.2	1.6	1.4	17
XNBR+DAP+Zn ²⁺		4.3±0.6	1.6±0.7	0.8	0.8	37
XNBR+DAP+Co ²⁺	1	10.3±1.1	3.3±0.6	2.1	1.9	32
XNBR+DAP+Ni ²⁺		8.6±0.9	2.2 ±1.3	1.6	1.6	26
XNBR+DAP+Zn ²⁺		4.3±0.6	2.6±1.2	0.8	1.2	59
XNBR+DAP+Co ²⁺	3	10.3±1.1	4.2±0.8	2.1	2.2	41
XNBR+DAP+Ni ²⁺		8.6±0.9	2.7±0.4	1.6	3.0	31
XNBR+DAP+Zn ²⁺		4.3±0.6	2.9±0.9	0.8	1.3	66
XNBR+DAP+Co ²⁺	6	10.3±1.1	5.3±1.3	2.1	2.3	52
XNBR+DAP+Ni ²⁺		8.6±0.9	3.6±0.4	1.6	1.6	42
XNBR+DAP+Zn ²⁺		4.3±0.6	3.2±0.9	0.8	1.1	73
XNBR+DAP+Co ²⁺	12	10.3±1.1	5.8±0.7	2.1	2.5	57
XNBR+DAP+Ni ²⁺		8.6±0.9	3.7±1.1	1.6	2.8	43
XNBR+DAP+Zn ²⁺		4.3±0.6	3.6±1.2	0.8	1.3	82
XNBR+DAP+Co ²⁺	24	10.3±1.1	9.1±1.3	2.1	2.4	88
XNBR+DAP+Ni ²⁺		8.6±0.9	4.8±1.1	1.6	2.3	56
XNBR+DAP+Zn ²⁺		4.3±0.6	4.4±1.2	0.8	1.3	100

Figure 8. The typical stress-strain plots of both pristine and healed sample of (a) XNBR+DAP+Co²⁺, (b) XNBR+DAP+Ni²⁺, and (c) XNBR+DAP+Zn²⁺.

Zn²⁺-DAP bond and Ni²⁺-DAP bond is not so dynamic as like the Co²⁺-DAP and Zn²⁺-DAP bond.

3.5.3. The different crosslinked systems on self-healing properties

We tabulated the self-healing properties of different metal-ligand coordination system of XNBR-DAP/Co²⁺, XNBR-DAP/Ni²⁺, and the XNBR-DAP/Zn²⁺ systems are shown in Figure 10.

Although XNBR-DAP/Zn²⁺ sample exhibits lower tensile strength, outstanding healing properties were observed, as the tensile strength 4.3±0.6 MPa (virgin sample) and 100% healing was obtained due to weak Zn-DAP bond and the insufficient metal-ligand cross-linking density form into the XNBR rubber. But in

XNBR-DAP/Co²⁺ sample exhibits both fairly good healing properties (88%) and very good mechanical strength (10.3±1.1 Mpa), due to strong Co-DAP dynamic bond and the good metal-ligand cross-linking. Whereas, XNBR-DAP/Ni²⁺ sample exhibit 8.6±0.9 MPa (medium) tensile strength and the 56% (lowest) healing efficiency, due to stronger Ni-DAP bond and sufficient metal-ligand crosslinking into the XNBR rubber.

3.6. The FTIR analysis of metal-ligand modified compounds after self-healing at 80°C for 24 hours

The FT-IR analysis has demonstrated the formation of a coordination bond between the DAP ligand and

Figure 9. The self-healing properties of (a) XNBR+DAP+Co²⁺, (b) XNBR+DAP+Ni²⁺, and (c) XNBR+DAP+Zn²⁺ samples.

Figure 10. The self-healing properties with different cross-linked systems.

Figure 11. The FT-IR spectra of various metal-ligand modified compounds after self-healing.

the various metal ion after self-healing at 80 °C for 24 hours. FT-IR spectra of the control sample (XNBR+DAP) and healed sample (XNBR+DAP+Co²⁺, XNBR+DAP+Ni²⁺, and XNBR+DAP+Zn²⁺) were shown in Figure 11. In the case of XNBR+DAP compound, the characteristic peak at 16161 and 1453 cm⁻¹ corresponds to the N–H bending and the C=C stretching vibration of free pyridine. The XNBR+DAP+Co²⁺ compound, the change of amide band I, and amide band II were recorded during the healing process. However, the amide band I was shifted to the lower wavenumber and the amide II was shifted to the higher wavenumber. In the case of XNBR+DAP+Co²⁺ compound, after 24 h self-healing at 80° C, the amide band I (C=O stretching) and amide band II (–N–H bending) were recorded at 1650 and 1672 cm⁻¹, with respect to that of the virgin sample. The peak at 1438 cm⁻¹, C=N stretching vibration of coordinated pyridine of the DAP ligand throughout the damage and healing process. The results showed that the various metal-ligand coordination bond was formed after self-healing. The healing ability was attributed to the dynamic bond between the Co²⁺ metal ion and the DAP ligand. Similarly, the dynamic behavior of XNBR+DAP+Ni²⁺ and XNBR+DAP+Zn²⁺ compounds were also happened and was shown in Figure 11.

3.7. Mechanism of self-healing of XNBR

created by the different metal-DAP bonds

The healing mechanism of XNBR rubber is tabulated by the intrinsic dynamic supramolecular metal-ligand coordination bonds at the damaged point and which is shown in Figure 12. The XNBR-DAP/Co²⁺, XNBR-DAP/Ni²⁺, and the XNBR-DAP/Zn²⁺ are used as a proposed model elastomer to tabulated the chemistry at the crack region changes during the fracture-repair cycle. In the case of a damaged specimen of XNBR-DAP/Zn²⁺ and XNBR-DAP/Co²⁺, the Zn-DAP bond is more weak and dynamic than the Co-DAP bond, because of, lower metal-ligand cross-linked density and rebonding after 24 hours at 80 °C of the healed sample. But in the case of XNBR-DAP/Ni²⁺ specimen, the Ni-pyridine bond is more strong as compare to the Co and Zn metal, in fracture sample the Ni-pyridine bond is not broken down (as shown in Figure 12) but Ni-DAP bonds are broken down and these bonds are rebonding after 24 hours at 80 °C of the healed sample.

3.8. Rheometric (MDR) study of XNBR rubber with various metal ions compounds

The rheometric analysis of all the rubber composites is shown in Figure 13. In the case of XNBR+DAP (without metal ion) compound, the storage modulus and loss modulus is almost similar, with no change

Figure 12. The schematic illustration of the scission and regeneration of the different metal-ligand bonds during self-healing.

Figure 13. The MDR study of various rubber composites (a) XNBR+DAP (without metal ion), (b) XNBR+Co²⁺, (c) XNBR+Ni²⁺, and (d) XNBR+Zn²⁺ compounds with metal ions.

in modulus value due to the absence of metal ion no cross-linking takes place in the polymer chain. The DAP ligand can only form the amide bond between the –COOH group of XNBR rubber and the –NH₂ group of DAP ligand and also confirmed in FT-IR analysis (Figure 2). Whereas XNBR rubber with various metal ions compounds, the storage modulus increases with time because of various metal ions and the –COOH group interaction takes place into a polymer matrix. So the metal-oxygen bonds in polymer chains are improved the mechanical as well as the rheometric properties.

3.9. Swelling study

The cross-link density of all the rubber composites is an analysis using swelling experiment techniques, which is shown in Figure 14. To compare the cross-link density of XNBR rubber cross-linked via various metal-ligand systems and the XNBR rubber with cross-linked only various metal ions, which is shown in Figure 14b. In the case of XNBR+DAP+Ni system, the cross-link density is very high compared to Co and Zn systems. Whereas various metal ions modified compounds are shows the less cross-linking density compared to metal-ligand rubber compounds,

Figure 14. The cross-link density of various rubber compounds (a) XNBR with various metal ions-ligand cross-link system and (b) XNBR rubber with various metal ions systems.

due to good metal-ligand interaction into the polymer backbone. But the XNBR+DAP compound is soluble in toluene, which indicated that DAP ligand could only form an amide bond between the $-\text{COOH}$ group and NH_2 group of the DAP ligand and that also confirmed from FT-IR analysis.

3.10. Optical microscopy study

The mending of the damaged surface of various samples was observed by using an optical microscope. The images of XNBR-DAP/ Zn^{2+} , XNBR-DAP/ Ni^{2+} , and XNBR-DAP/ Co^{2+} samples were compared after 24 h of a healing process that carried out at 80°C (Figure 15). The width of the damaged surface is noticeably reduced, presumably due to the highly dynamic metal-ligand coordination bonding that exists with the XNBR-DAP/metal system. The reference sample Figures 15a and 15b, which is not healed before and after the healing process at 80°C temperature for 24 hours.

3.11. Atomic force microscopy (AFM) study

The mending of the damaged surface of XNBR+DAP+ Zn^{2+} sample, which exhibits 100% healing efficiency, was followed by AFM study. The probe microscopic images, that take over the damaged surface of the sample, were compared after the

whole mending period (Figure 16). The XNBR+DAP+ Zn^{2+} compound exhibits the best healing efficiency and hence we have taken the only XNBR+DAP+ Zn^{2+} sample for the AFM study. The image shows that the compound is clearly healed after treatment at 80°C for 24 hours. The optical microscopic (Figure 15) and AFM study prove that the XNBR+DAP+ Zn^{2+} specimen was completely healed after 24 h at 80°C due to a highly dynamic metal-ligand bond formation.

3.12. Scanning electron microscopy (SEM) study

The morphology study of a fractured surface of pristine XNBR (a), the pure DAP particle (b), XNBR+DAP (c), XNBR+DAP+ Co^{2+} (d), XNBR+DAP+ Ni^{2+} (e), and the XNBR+DAP+ Zn^{2+} (f) compounds are shown in Figure 17. In the image of XNBR+DAP without metal ions, the ligand particles are uniformly dispersed into the matrix. But after the addition of various metal ion into the rubber matrix, to form good metal-ligand coordination, which is clearly observed into the images (Figure 17d, 17e, and 17f). In the image of XNBR+DAP+ Co^{2+} , XNBR+DAP+ Ni^{2+} , and XNBR+DAP+ Zn^{2+} with the different metal ions, the ligand particles, and the metal ions are thickly and uniformly dispersed into

Figure 15. The optical microscope images of XNBR+DAP (Reference sample) XNBR-DAP/ Ni^{2+} , XNBR-DAP/ Co^{2+} , and the XNBR-DAP/ Zn^{2+} sample before healing (a, c, e, and g) and the XNBR+DAP XNBR-DAP/ Ni^{2+} , XNBR-DAP/ Co^{2+} , and the XNBR-DAP/ Zn^{2+} sample after healing (b, d, f, and h) and the red arrow is indicated the cut marked.

the matrix. The good interaction of DAP ligand with various metal ions into the XNBR matrix gives better mechanical properties and good self-healing behavior. The good metal-ligand interaction and dispersion in the matrix are clearly observed in the figure.

Energy dispersive X-ray (EDX) study

The energy dispersive X-ray study of a fractured surface (a) XNBR+DAP, (b) XNBR+DAP+ Co^{2+} , (c) XNBR+DAP+ Ni^{2+} , and (d) XNBR+DAP+ Zn^{2+}

compounds are shown in Figure 18. From the EDX analysis, it clearly observed that various metal ions are present into metal-ligand modified rubber composites, but in the case of XNBR+DAP compound, the metal ion is absent.

3.13. High-resolution transmission electron microscopy (HR-TEM) study

The morphology study of XNBR+DAP, XNBR+DAP+ Co^{2+} , XNBR+DAP+ Ni^{2+} , and the

R1
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Figure 16. The AFM image of XNBR+DAP+Zn²⁺ sample. (a) and c) before and b) and d) after healing).

Figure 17. The SEM images of pristine XNBR (a), (b) the pure DAP particle, (c) XNBR+DAP, (d) XNBR+DAP+Co²⁺, (e) XNBR+DAP+Ni²⁺, and (f) the XNBR+DAP+Zn²⁺ compounds.

Figure 18. The EDX analysis of XNBR+DAP (a), XNBR+DAP+Co²⁺ (b), XNBR+DAP+Ni²⁺ (c) and (d) XNBR+DAP+Zn²⁺ compounds.

XNBR+DAP+Zn²⁺ are shown in Figure 19. In the image of XNBR+DAP compound, the ligand particles are uniformly dispersed and easily seen into a rubber matrix. After the addition of various metal ions on the XNBR+DAP system, the structure changes due to metal-ligand interaction, to form good metal-ligand coordination and well dispersion of the various metal ions and DAP ligands into rubber matrix, which is clearly observed into images (b, c, and d). The TEM image shows that good interaction of DAP ligand with various metal ions into the XNBR matrix gives better mechanical properties and good self-healing behavior. The SEM (Figure 17)

and TEM analysis are strong evidence that well dispersion and good coordination of various metal ions and ligand particles.

4. Conclusions

In this study, we have demonstrated a new self-healing rubber based on the metal-ligand coordination between DAP ligand and different metal ions (Co²⁺, Ni²⁺, and Zn²⁺) moieties incorporated into the XNBR backbone. The formation of amide linkage and metal-ligand coordination bonds into the rubber backbone is confirmed by the FTIR analysis. The strength of the different metal ion-DAP ligand coordination

Figure 19. The TEM images of XNBR+DAP (a), XNBR+DAP+Co²⁺ (b), XNBR+DAP+Ni²⁺ (c) and (d) XNBR+DAP+Zn²⁺ compounds.

bonds depends on the type of metal ions. The self-healing ability of rubber composite is mainly determined by the lability and dynamic nature of metal-ligand bonds. We found that XNBR-DAP/Zn²⁺ compound exhibited the 100% healing efficiency with the tensile strength of 4.3 ± 0.6 MPa because of very dynamic character of Zn-DAP bond and XNBR-DAP/Co²⁺ sample showed a good healing efficiency of 88% with excellent tensile strength of 10.3 ± 1.1 MPa, due to the dynamic feature of Co-DAP bond. While for the XNBR-DAP/Ni²⁺ compound, the poor healing efficiency is noticed because of the strong Ni-DAP bond and after self-healing,

the metal-ligand coordination bond was formed. This finding is confirmed by the DSC, FTIR and the stress relaxation (RPA 2000) results reported in this work. The approach of changing commercial rubber into the self-healing purpose by developing multiple metal-ligand crosslinking networks and which is the new technologies for the acceptable application of the cross-linked rubber products. The various metal-DAP bonds are in stumble during healing, after that the metal ion is still joined to the ligand by the strong metal-pyridine bond and which is permitting the carboxylated nitrile rubber with the quick and excellent self-healing capability.

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References

- [1] Liu J., Wang S., Tang Z., Huang J., Guo B., Huang G.: Bioinspired engineering of two different types of sacrificial bonds into chemically cross-linked cis-1,4-polyisoprene toward a high-performance elastomer. *Macromolecules*, **49**, 8593–8604 (2016). <https://doi.org/10.1021/acs.macromol.6b01576>
- [2] Bartlett M. D., Dickey M. D., Majidi C.: Self-healing materials for soft-matter machines and electronics. *NPG Asia Materials*, **11**, 21/1–21/4 (2019). <https://doi.org/10.1038/s41427-019-0122-1>
- [3] Li G., Xiao P., Hou S., Huang Y.: Graphene based self-healing materials. *Carbon*, **146**, 371–387 (2019). <https://doi.org/10.1016/j.carbon.2019.02.011>
- [4] Wang Z., Xie C., Yu C., Fei G., Wang Z., Xia H.: A facile strategy for self-healing polyurethanes containing multiple metal–ligand bonds. *Macromolecular Rapid Communications*, **39**, 1700678/1–1700678/7 (2018). <https://doi.org/10.1002/marc.201700678>
- [5] Qiao H., Qi P., Zhang X., Wang L., Tan Y., Luan Z., Xia Y., Li Y., Sui K.: Multiple weak H-bonds lead to highly sensitive, stretchable, self-adhesive, and self-healing ionic sensors. *ACS Applied Materials and Interfaces*, **11**, 7755–7763 (2019). <https://doi.org/10.1021/acsami.8b20380>
- [6] White S. R., Sottos N. R., Geubelle P. H., Moore J. S., Kessler M. R., Sriram S. R., Brown E. N., Viswanathan S.: Autonomic healing of polymer composites. *Nature*, **409**, 794–797 (2001). <https://doi.org/10.1038/35057232>
- [7] Kim C., Ejima H., Yoshie N.: Polymers with autonomous self-healing ability and remarkable reprocessability under ambient humidity conditions. *Journal of Materials Chemistry A*, **6**, 19643–19652 (2018). <https://doi.org/10.1039/C8TA04769c>
- [8] D’Elia E., Eslava S., Miranda M., Georgiou T. K., Saiz E.: Autonomous self-healing structural composites with bio-inspired design. *Scientific Reports*, **6**, 25059/1–25059/11 (2016). <https://doi.org/10.1038/srep25059>
- [9] Toohey K. S., Sottos N. R., Lewis J. A., Moore J. S., White S. R.: Self-healing materials with microvascular networks. *Nature Materials*, **6**, 581–585 (2007). <https://doi.org/10.1038/nmat1934>
- [10] Peng Y., Zhao L., Yang C., Yang Y., Song C., Wu Q., Huang G., Wu J.: Super tough and strong self-healing elastomers based on polyampholytes. *Journal of Materials Chemistry A*, **6**, 19066–19074 (2018). <https://doi.org/10.1039/C8TA06561f>
- [11] Liu Y., Li Z., Liu R., Liang Z., Yang J., Zhang R., Zhou Z., Nie Y.: Design of self-healing rubber by introducing ionic interaction to construct a network composed of ionic and covalent cross-linking. *Industrial and Engineering Chemistry Research*, **58**, 14848–14858 (2019). <https://doi.org/10.1021/acs.iecr.9b02972>
- [12] Xu C., Nie J., Wu W., Zheng Z., Chen Y.: Self-healable, recyclable, and strengthened epoxidized natural rubber/carboxymethyl chitosan biobased composites with hydrogen bonding supramolecular hybrid networks. *ACS Sustainable Chemistry and Engineering*, **7**, 15778–15789 (2019). <https://doi.org/10.1021/acssuschemeng.9b04324>
- [13] Terryn S., Brancart J., Lefebvre D., Van Assche G., Vanderborght B.: Self-healing soft pneumatic robots. *Science Robotics*, **2**, ea4268/1–ea4268/12 (2017). <https://doi.org/10.1126/scirobotics.a4268>
- [14] Habault D., Zhang H., Zhao Y.: Light-triggered self-healing and shape-memory polymers. *Chemical Society Reviews*, **42**, 7244–7256 (2013). <https://doi.org/10.1039/C3CS35489J>
- [15] Hinton Z. R., Shabbir A., Alvarez N. J.: Dynamics of supramolecular self-healing recovery in extension. *Macromolecules*, **52**, 2231–2242 (2019). <https://doi.org/10.1021/acs.macromol.8b02423>
- [16] Moniruzzaman M., Christogianni P., Kister G.: Self-healing in epoxy thermoset polymer films triggered by UV ILight. *Procedia Engineering*, **148**, 114–121 (2016). <https://doi.org/10.1016/j.proeng.2016.06.472>
- [17] Amamoto Y., Kamada J., Otsuka H., Takahara A., Matyjaszewski K.: Repeatable photoinduced self-healing of covalently cross-linked polymers through reshuffling of trithiocarbonate units. *Angewandte Chemie - International Edition*, **50**, 1660–1663 (2011). <https://doi.org/10.1002/anie.201003888>
- [18] Rekondo A., Martin R., Ruiz de Luzuriaga A., Cabañero G., Grande H. J., Odriozola I.: Catalyst-free room-temperature self-healing elastomers based on aromatic disulfide metathesis. *Materials Horizons*, **1**, 237–240 (2014). <https://doi.org/10.1039/C3MH00061c>
- [19] Yang Y., Urban M. W.: Self-healing of polymers *via* supramolecular chemistry. *Advanced Materials Interfaces*, **5**, 1–19 (2018). <https://doi.org/10.1002/admi.201800384>
- [20] Pal S., Das M., Naskar K.: Exploring copper–amino acid complexes in cross-linking of maleated ethylene propylene rubber. *Industrial and Engineering Chemistry Research*, **58**, 17802–17813 (2019). <https://doi.org/10.1021/acs.iecr.9b03254>
- [21] Nomimura S., Osaki M., Park J., Ikura R., Takashima Y., Yamaguchi H., Harada A.: Self-healing alkyl acrylate-based supramolecular elastomers cross-linked *via* host–guest interactions. *Macromolecules*, **52**, 2659–2668 (2019). <https://doi.org/10.1021/acs.macromol.9b00471>

- [22] Hou J-B., Zhang X-Q., Wu D., Feng J-F., Ke D., Li B-J., Zhang S.: Tough self-healing elastomers based on the host–guest interaction of polycyclodextrin. *ACS Applied Materials and Interfaces*, **11**, 12105–12113 (2019). <https://doi.org/10.1021/acsami.9b00626>
- [23] Xu C., Cao L., Huang X., Chen Y., Lin B., Fu L.: Self-healing natural rubber with tailorable mechanical properties based on ionic supramolecular hybrid network. *ACS Applied Materials and Interfaces*, **9**, 29363–29373 (2017). <https://doi.org/10.1021/acsami.7b09997>
- [24] Das A., Sallat A., Böhme F., Suckow M., Basu D., Wießner S., Stöckelhuber K. W., Voit B., Heinrich G.: Ionic modification turns commercial rubber into a self-healing material. *ACS Applied Materials and Interfaces*, **7**, 20623–20630 (2015). <https://doi.org/10.1021/acsami.5b05041>
- [25] Kammakam I., O’Harra K. E., Dennis G. P., Jackson E. M., Bara J. E.: Self-healing imidazolium-based ionene-polyamide membranes: An experimental study on physical and gas transport properties. *Polymer International*, **68**, 1123–1129 (2019). <https://doi.org/10.1002/pi.5802>
- [26] Cui X., Song Y., Wang J-P., Wang J-K., Zhou Q., Qi T., Li G. L.: Self-healing polymers with tunable mechanical strengths *via* combined hydrogen bonding and zinc-imidazole interactions. *Polymer*, **174**, 143–149 (2019). <https://doi.org/10.1016/j.polymer.2019.04.060>
- [27] Li G., Xiao P., Hou S., Huang Y.: Rapid and efficient polymer/graphene based multichannel self-healing material *via* Diels–Alder reaction. *Carbon*, **147**, 398–407 (2019). <https://doi.org/10.1016/j.carbon.2019.03.021>
- [28] Oh C-R., Lee S-H., Park J-H., Lee D-S.: Thermally self-healing graphene-nanoplate/polyurethane nanocomposites *via* Diels–Alder reaction through a one-shot process. *Nanomaterials*, **9**, 434–346 (2019). <https://doi.org/10.3390/nano9030434>
- [29] Behera P. K., Mondal P., Singha N. K.: Self-healable and ultrahydrophobic polyurethane-poss hybrids by Diels–Alder ‘click’ reaction: A new class of coating material. *Macromolecules*, **51**, 4770–4781 (2018). <https://doi.org/10.1021/acs.macromol.8b00583>
- [30] Latif S., Amin S., Haroon S. S., Sajjad M. I. A.: Self-healing materials for electronic applications: An overview. *Materials Research Express*, **6**, 062001/1–062011/6 (2019). <https://doi.org/10.1088/2053-1591/ab0f4c>
- [31] Du G., Mao A., Yu J., Hou J., Zhao N., Han J., Zhao Q., Gao W., Xie T., Bai H.: Nacre-mimetic composite with intrinsic self-healing and shape-programming capability. *Nature Communications*, **10**, 1–8 (2019). <https://doi.org/10.1038/s41467-019-08643-x>
- [32] Zhang B., Zhang W., Zhang Z., Zhang Y-F., Hingorani H., Liu Z., Liu J., Ge Q.: Self-healing four-dimensional printing with an ultraviolet curable double-network shape memory polymer system. *ACS Applied Materials and Interfaces*, **11**, 10328–10336 (2019). <https://doi.org/10.1021/acsami.9b00359>
- [33] Cheng Z., Yan M., Cao L., Huang J., Cao X., Yuan D., Chen Y.: Design of nitrile rubber with high strength and recycling ability based on Fe³⁺–catechol group coordination. *Industrial and Engineering Chemistry Research*, **58**, 3912–3920 (2019). <https://doi.org/10.1021/acs.iecr.8b05993>
- [34] Cheng B., Lu X., Zhou J., Qin R., Yang Y.: Dual cross-linked self-healing and recyclable epoxidized natural rubber based on multiple reversible effects. *ACS Sustainable Chemistry and Engineering*, **7**, 4443–4455 (2019). <https://doi.org/10.1021/acssuschemeng.8b06437>
- [35] Vermonden T., van der Gucht J., de Waard P., Marcelis A. T. M., Besseling N. A. M., Sudhölter E. J. R., Fleer G. J., Cohen Stuart M. A.: Water-soluble reversible coordination polymers: Chains and rings. *Macromolecules*, **36**, 7035–7044 (2003). <https://doi.org/10.1021/ma030353t>
- [36] Jiang F., Zhang X., Hwang W., Briber R. M., Fang Y., Wang H.: Supramolecular luminescent triblock copolymer thermoplastic elastomer *via* metal-ligand coordination. *Polymer Testing*, **78**, 105956/1–105956/8 (2019). <https://doi.org/10.1016/j.polymertesting.2019.105956>
- [37] Zhang X., Tang Z., Guo B., Zhang L.: Enabling design of advanced elastomer with bioinspired metal–oxygen coordination. *ACS Applied Materials and Interfaces*, **8**, 32520–32527 (2016). <https://doi.org/10.1021/acsami.6b10881>
- [38] Basu D., Das A., Stöckelhuber K. W., Jehnichen D., Formanek P., Sarlin E., Vuorinen J., Heinrich G.: Evidence for an *in situ* developed polymer phase in ionic elastomers. *Macromolecules*, **47**, 3436–3450 (2014). <https://doi.org/10.1021/ma500240v>
- [39] Trivedi M. K., Branton A., Trivedi D., Nayak G., Mishra R., Jana S.: Characterization of physical, thermal and spectral properties of biofield treated 2-aminopyridine. *Science Journal of Analytical Chemistry*, **3**, 127–134 (2015). <https://doi.org/10.11648/j.sjac.20150306.18>
- [40] Mamo A., Finocchiaro P., Bottino F., Pappalardo S.: Synthesis and characterization of polyamides and polyureas with acyclic and cyclic bipyridinediyl diamino structures in the polymer backbone. *Journal of Polymer Science Part A: Polymer Chemistry*, **28**, 2237–2247 (1990). <https://doi.org/10.1002/pola.1990.080280901>