DYNAMIC REVERSIBLE NETWORKS AND DEVELOPMENT OF SELF-HEALING RUBBERS: A CRITICAL REVIEW

SUBHRADEEP MANDAL,[1,2] AMIT DAS,[1,*] ERIC EUCHLER,[1] SVEN WIESSNER,[1,2] GERT HEINRICH,[2] JUN SAWADA,[3] RYOJI MATSUI,[3] TAKAYUKI NAGASE,[3] TOSHIO TADA[3]

[1]LEIBNIZ-INSTITUT FÜR POLYMERFORSCHUNG DRESDEN E.V., DRESDEN, GERMANY
[2]TECHNISCHE UNIVERSITÄT DRESDEN, DRESDEN, GERMANY
[3]SUMITOMO RUBBER INDUSTRIES LTD., KOBE, JAPAN

RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 96, No. 2, pp. 175–195 (2023)

ABSTRACT

An intensive literature search shows that research in the field of self-healing rubbers is still in its infancy. By analyzing the various reviews and reports available, most of the results prove to be complicated; however, a few studies show promising self-healing properties of new elastomers. Most of these materials were prepared by relatively sophisticated chemical syntheses. Many of the studies on self-healing materials also deal with commercial rubbers, but the mechanical performance of these self-healing systems is very poor for practical application, perhaps because self-healing systems are usually prepared with an uncured or pseudo-crosslinked matrix structure. The poor mechanical properties are related to the highly viscous but inelastic nature of the uncured or only partially cured rubber compound. Importantly, most of the studies have been conducted on rubber systems without reinforcing fillers. For filler-reinforced rubber systems, the question is whether the working principle of reversible bonds is applicable. This literature review attempted to compile the current promising self-healing systems, describe their underlying chemical mechanisms, and discuss the self-healing concept from a thermodynamic perspective. In addition, this review is focused on the critical discussion of the principle and origin of self-healing behavior and finally draws conclusions on the applications and opportunities for further developments in this field. [doi:10.5254/rct.23.76967]

INTRODUCTION

DEFINITION OF SELF-HEALING

The term "self-healing" often appears in biology. For example, if a living being cuts its hand, the body immediately begins to heal itself, which is an example of the self-healing mechanism in action. This biological activity ensures the continuation of life and is one of the most essential characteristics of lifeforms. Therefore, material scientists strive to impregnate this living character into a lifeless object or material. By definition, this character can be expressed as the ability of a material to heal (or repair) damage automatically and autonomously, i.e., without external intervention.[1] In practice, however, external intervention is required to repair the damage to material systems. Depending on the process, there are two types of self-healing mechanisms. The first mechanism is autonomous self-healing, wherein the self-healing process does not require external stimuli. The second mechanism is so-called non-autonomous self-healing in which various external stimuli are required, such as temperature, pressure, or electrical power.

Other definitions of self-healing can be found in the literature, stating that "A polymer displaying self-healing properties needs the ability to transform physical energy into a chemical response for the healing of damage."[2] In this process, the original damage creates a free (usually fresh) interface (observed as a crack) that in turn can serve as a site for molecular processes, such as swelling, patching, or simple molecular diffusion. These activities can eventually trigger a welding process.

The above-mentioned definitions, however, do not include the primary qualities or criteria of the self-healing process. There are four basic categories in a self-healing process.[3] (i) localized or

---

*Corresponding author. Ph: +49 3514658579; email: das@ipfdd.de

area-specific phenomenon, in which the molecular processes should be directed to the site where the cut or tear formed; (ii) temporality or time dependence, which is required for bond reformation; (iii) mobility or transport, wherein a network structure is required to transfer healing bonds to the damaged areas and the chains must be mobile enough to cause diffusion; and (iv) a specific process by which self-healing occurs. For example, Diels–Alder,[4] reversible metathesis,[5] hydrogen bonding,[6] and many more specific processes are capable of self-healing. However, definition and quantification are by no means straightforward, because the term self-healing generally refers to a biologically induced process. In this context, Das et al. described that "Self-healing being a biological term, the proper definition of this property is still to be established. Efforts also should be given to quantify the 'self-healing' efficiency in a more scientific manner."[7] In the literature many reports can be found where the self-healing efficacy is estimated by studying stress–strain properties of the system. The percentage of retention of the stress–strain properties, for example, tensile strength and elongation at break, after cut and mending experiments is considered.

MIMICKING THE CONCEPTS OF SELF-HEALING FROM NATURE

If we look at biological systems, we can get an idea of how self-healing actually takes place. When there is a cut or a wound in the human body, there is a localization or identification of the area of the cut. Then comes temporality, which states that the healing process requires time to be effective. For the purpose of healing, the human vascular system transports special blood cells to the injured area. Platelets are components of blood cells that are responsible for repairing damaged blood vessels by activating the coagulation cascade and forming a platelet plug at the damaged site. During the self-healing process, fibrin plays an important role in sticking and binding the damaged site for healing. Because self-healing is a biological concept, we can only mimic the natural phenomenon.[2] We can also correlate the natural phenomenon with the reported self-healing mechanisms. The self-healing compounds consist of microcapsules and microvascular components that contain healing agents are also similar to those of the human body and plant healing. The concept of dynamic crosslinking may also have some relationship to our DNA repair phenomenon. Finally, the concept of metal ion coordination for self-healing comes from marine mussels. Marine mussels are most commonly found near rocky seashores. They live in a region where smashing waves are common. The sticky ends of the byssal threads are the key to their dominance, and there is a rare amino acid called l-dopa (3,4-dihydroxy-phenylalanine) that plays an important role in this adherence. Divalent metal ions (Cu, Zn, Ni) have the property of coordinating with proteins. In addition, the proteins can form hydroxyl group bonds with the rocks. However, the mechanism is very complicated and still not well understood, but the metal ion coordination in self-healing is adopted by this concept.[8,9]

THERMODYNAMICS OF SELF-HEALING: ENTANGLEMENT, DIFFUSION, AND MOLECULAR WEIGHT DEPENDENCE

Molecules with shorter chain lengths have higher mobility than large molecules, thus interactions between active self-healing sites and shorter chain-length molecules are more likely. By contrast, the dimensional stability is higher with longer chain-length molecules. This indicates that to get material with good dimensional stability as well as good self-healing properties, there should be some critical chain length, where the balance of the two properties is well maintained.[10] The mobility of the molecular chain at the interface should be discussed in line with the chemical self-healing mechanisms because any rubbery material exhibits some physical behavior, which can be associated with self-healing, such as entanglements in the chain, diffusion of the chains, flow of the uncured part, and sometimes radical combination. All of these factors contribute to the natural entropy-driven mixing process of the material; however, adequate mechanical properties and creep resistance cannot be achieved during healing with this type of flowing process. It is necessary to have an anchoring point in the matrix that can retain the chains or entanglements in place. Nevertheless, to carry out a self-healing process, other factors, such as diffusion and entanglements, must also be involved. To understand the thermodynamics of self-healing, it is important to understand the viscoelastic properties of a polymer as well as the diffusion of the polymer chains at molecular scales. In this regard, an understanding of the polymer reptation model would be beneficial.[11,12] Although the details of the reptation model are outside of the scope of this report, from the perspective of self-healing, it is evident that the polymer chains must be diffused out from the tubes to have a sufficient repairing capacity of the material. There are two timeframes that exist for this particular phenomenon: one timeframe is short-range wriggling motion, which is proportional to the square of the molecular weight (Eq. 1) and the other timeframe is the total time to disengage from the tube, which is proportional to the cube of the molecular weight (Eq. 2). It can be stated with certainty that lower molecular weight polymers, in general, exhibit more favorable repairing modes than the higher molecular weight polymers:[13]

$$T_e \propto M^2 \tag{1}$$

$$T_r \propto M^3 \tag{2}$$

where T_e is the short short-range wriggling motions, T_r is the amount of time for a chain to disengage from the tube, and M is the average molecular weight of the polymer.

These relaxation periods and reptation dynamics can differ based on the elastomer's network structure, such as a permanently crosslinked elastomer and an elastomer with reversible bonds. The latter structure can be defined as flexible bonds with a controlled length that can be varied. In addition, the kinetics of these reversible bonds is strongly force dependent.[14] These bonds are located in an elastomer's side chain, which contains the associating ionic groups responsible for the material's self-healing. According to a recent article, the friction in an elastomeric matrix can increase due to the reversible bonding and ionic association, resulting in the slowing down of the reptation dynamics of the polymer chains.[15] In this report, a reptation model that is the modified version of the so-called slip-link model was presented and solved for the relaxation modulus.[11,16] The effects of entanglements and reversible crosslinkers are modeled as a discrete form of constraints that influence the motion of the primitive path. In contrast to a non-associating entangled system, the model calculations demonstrate that the elastic modulus has a much higher first plateau and a delayed terminal relaxation. These effects are attributed to the evolution of the entangled chains as influenced by tethered reversible linkers. The model is solved for the case when linker survival time τ_s is greater than the entanglement time (τ_e), but less than the Rouse time ($\tau_{R;}\ \tau_e < \tau_s < \tau_R$).[15]

If diffusion is considered, the diffusion coefficient (D) is inversely proportional to the square of molecular weight, which again favors lower molecular weight polymers:

$$D \,\alpha\, 1/M^2 \tag{3}$$

In the case of fracture stress (σ), low molecular weight polymers also have faster mending times and more energetically favorable stress recoveries:[13]

$$\sigma \propto (t/M)1/40 < t < T_r \tag{4}$$

Furthermore, enthalpic and entropic contributions are also relevant in terms of self-healing properties. Following a crack formation in the system, it generally attains a non-equilibrium state. However, self-healing will occur in a new Gaussian-equilibrium state by the reversible bonds.

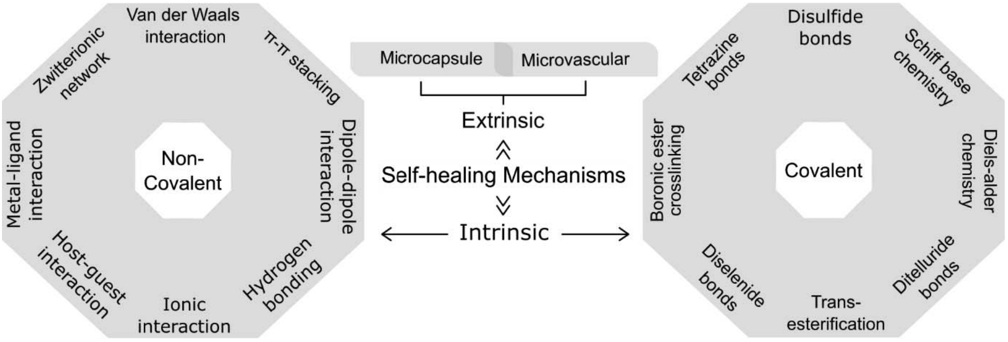

FIG. 1. — Schematic representation of molecular mechanisms involved in self-healing.

Energetically, self-repair will occur when the Gibbs free energy (ΔG) is less than 0:

$$\Delta G = \Delta H - T\Delta S < 0 \tag{5}$$

$$\text{with } \Delta S = S_2 - S_1 = k \cdot \ln(\Omega_2/\Omega_1) \tag{6}$$

where H is enthalpy, S is entropy, T is temperature, Ω_1 and Ω_2 are the numbers of available arrangements of chain segments, and k is the Boltzmann constant.

In principle, in a polymer with a low glass transition temperature (T_g) and low molecular weight (M), the chains are mobile, and the entropy is high. By contrast, higher molecular weight polymer chains are more entangled with lower entropic state and the mobility of the chains are highly restricted.[13] If we consider the influence of temperature on entropy, at a higher temperature the entropy is higher. Notably, temperature is an external stimulus, and it is generally applied to support self-healing. External stimuli are generally required to overcome the positive G when self-healing events are endothermic ($\Delta H > 0$) or a polymer network is too stiff to perform conformational changes ($\Delta S < 0$). The most effective self-healing may be obtained in the case of exothermic recoupling, such as radical recoupling or hydrogen bonding.[13]

MECHANISMS OF SELF-HEALING

The self-healing mechanisms consist of two main types: extrinsic and intrinsic (Figure 1). The healing agent is generally isolated from the main compounding recipe in extrinsic self-healing, such as in different microcapsules. The healing agent is released from the microcapsules in the damaged zone, and the mending takes place through chemical reaction. The advantage of an extrinsic approach is that it enables the repair of rather extensive areas of damage. However, because the healing agent is depleting in one healing process, repetitive healing is no longer possible in this case.[17] Nevertheless, for multiple healing processes, there is another similar type of mechanism called the microvascular system. In this system, a network of capillaries is incorporated into the elastomeric system and the healing agent can continuously flow through them in the damaged area. Intrinsic mechanisms generally rely on the chemical networks through molecular level mechanisms such as dynamic bonds, ionic aggregation, or hydrogen bond formation. These intrinsic mechanisms are always supposed to be reversible and can be effective in multiple healing events.[18] The intrinsic mechanisms can be classified into two main categories: non-covalent reversible interactions and covalent interactions. The following section clarifies the categorization of self-healing mechanisms (Figure 1; Table I).[3]

TABLE I
REVERSIBLE NETWORK MECHANISMS FROM LITERATURE

No.	Mechanism	References
1	Microcapsule	19, 20
2	Microvascular system	21, 22
3	Van der Waals interaction	23, 24
4	π-π Stacking	25, 26
5	Dipole–dipole interaction	27, 28
6	Hydrogen bond formation	6, 29
7	Ionic interaction	30–32
8	Host–guest interaction	33, 34
9	Metal–ligand interaction	35–37
10	Zwitterionic network	38, 39
11	Disulfide bonds	5, 40
12	Schiff-base chemistry	41, 42
13	Diels–Alder chemistry	4, 43, 44
14	Ditelluride bonds	45, 46
15	Transesterification	47, 48
16	Diselenide bonds	49, 50
17	Boronic ester bonds	51–53
18	Tetrazine bonds	54, 55

SELF-HEALING MECHANISMS

EXTRINSIC MECHANISM

In the microcapsule mechanism, the healing agent is released from the microcapsules in the damaged zone and the mending takes place through the polymerization reaction (Figure 2a). White et al. discussed this microcapsule mechanism, which is recognized as the first generation self-healing concept.[56] In this case, the microcapsule is made of urea formaldehyde resin and this resin

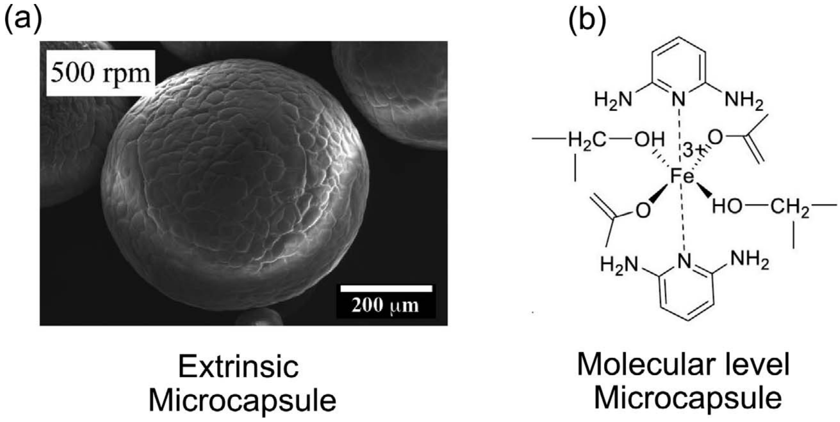

FIG. 2. — Different types of microcapsules: (a) extrinsic microcapsule formed at 500 rpm agitation rate (reproduced with permission from ref 20, Copyright 2008 American Chemical Society) and (b) molecular level microcapsule (reproduced with permission from ref 35, Copyright 2021 American Chemical Society).

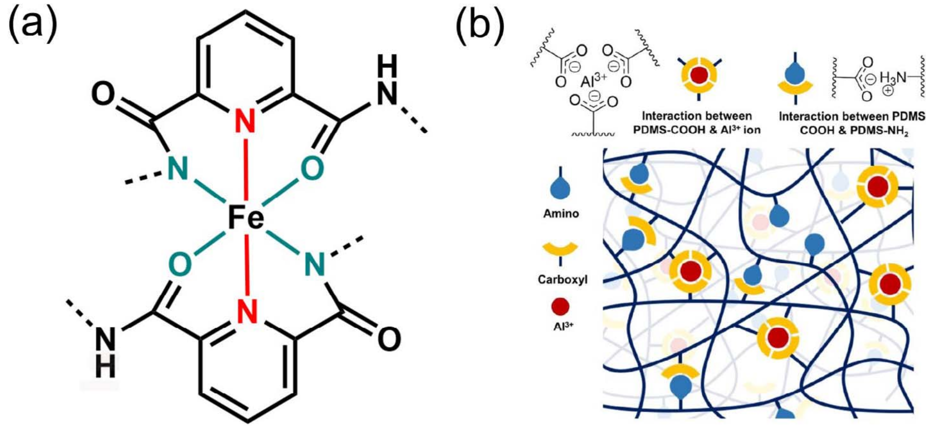

FIG. 3. — Different metal ion coordination mechanisms: (a) three different types of coordination bonds with Fe and 2,6-pyridinedicarboxamide ligand and (b) metal ion coordination with carboxyl- and amine-grafted PDMS (reproduced with permission from ref 57, Copyright 2021 American Chemical Society).

shell contains the actual healing agent inside the capsule. The healing agent is the diene polymer dicyclopentadiene. The final component in this system is a polymerization catalyst or healing trigger called the Grubb's catalyst, which is a transition metal carbene complex. Now the healing agent can be released from the microcapsule by capillary action and polymerize itself in the crack area with the aid of the catalyst. This polymerization or healing is irreversible and only active for one healing event.[20] However, the idea of a microcapsule has evolved from an extrinsic mechanism to in situ–generated molecular level microcapsules over time.

Recently, molecular level microcapsules were studied for the self-healing of epoxidized NR (ENR).[35] The mechanism (Figure 2b) is discussed in detail in the forthcoming section.

INTRINSIC MECHANISMS

Metal Ion Coordination in Elastomer Matrix. — The metal ion coordination concept of self-healing can be found in natural marine mussels around rocky sea shorelines. The sticky ends of byssal threads of the mussels contain a rare amino acid called l-dopa (or 3,4-dihydroxy-phenylalanine) that can coordinate with divalent metal ions, such as copper, zinc, and nickel. These protein fragments can also establish a reversible bond with the rocks.[8,9] Inspired by this concept from nature, a polydimethylsiloxane (PDMS) system was developed using a complexing agent called 2,6-pyridinedicarboxamide. This complexing agent is capable of creating three types of bonds with the metal ion: a strong iron–pyridyl bond and two weaker carboxamido–iron bonds through coordination linkage (Figure 3a). The binding energy of the first bond resembles a covalent interaction, whereas the other two bonds are weaker, like hydrogen bonds, and are stable only due to a strong chelating effect. The weak bonds could dissolve and reform at any time due to the reversible metal–ligand interaction. However, the final mechanical properties of such composites were found to be very poor; for example, the tensile strength of the composite was only in the range of kilopascals.[58] This kind of approach was also accomplished when PDMS was grafted with carboxyl groups as well as with amine groups and then the system was treated with Al^{3+}. This treatment results in the combination of an ionic bond between amine and the carboxylic group and a coordination bond between Al^{3+} and the carboxylic group (Figure 3b). Finally, it was reported that the coordination bond was responsible for the dimensional stabilities and mechanical performance, whereas the ammonium–carboxylate linkage acted as a reversible weak bond. However, the final mechanical properties were inferior as found in previous work.[57]

Metal ion coordination linkage in polymers not only improves the self-healing ability but also provides functional properties that can be used in many other applications, such as optics and sensors.[59] This scenario, based on the metal ion complexes in elastomers without a d-block transition metal, has not yet been studied in detail. Exploration of dual metal ion network formation in polymers by using two different metal ions, such as aluminum (Al^{3+}) and fluorescent europium (Eu^{3+}), is also reported. These metal ions were allowed to be reacted with two separate functional groups of the polymer that acted as ligands.

In this work, a copolymer was synthesized using ether methacrylate (MEO_2MA) and glycidyl methacrylate (GMA), i.e., P(MEO_2MA-co-GMA). However, for the coordination of metal ions, further grafting of acrylic acid (AA) and iminodiacetic acid (IDA) was required. In this case, IDA was selected carefully as a ligand of Eu^{+3} coordination because it could react with the oxirane ring of glycidyl methacrylate and simultaneously other parts of the molecule could form coordination linkage with the europium ion. Furthermore, the carboxyl group of AA was required to coordinate Al^{+3} metal ions. Eventually, an interpenetrating polymer network (IPN) was prepared by synthesizing iminodiacetic acid grafted– and AA-incorporated copolymers such as (MEO_2MA-co-IDHPMA) and P(MEO_2MA-co-AA).

Moreover, it was reported that ionic Al–COOH bond was responsible for the incorporation of strong polymer networks that mainly contributed to the mechanical properties and robustness of the IPN. In addition, Eu-iminodiacetate coordination imparted the dynamic reversible character in the network that dominated the elasticity, self-healing, and luminescence of the polymer. Finally, the materials offered 6.5 MPa of tensile strength and 90% self-healing efficiency. Also, it was observed that the self-healing efficiency could be tunable, depending on the controlled coordination ratio of the Eu^{3+} ion. The regulated thermo-reversibility of europium coordination also led the IPN to show luminescence properties such as europium-centered rapid on-or-off switchable red emission.[59]

Although metal ion coordination can be achieved in a variety of functional elastomers, some commercially available elastomers can also be used according to this principle without further chemical modification. Some examples are NBR, XNBR, and ENR. To facilitate the coordination bond formation between the available functional groups of the rubber with different metal ions, the use of ionic liquid is reported.[60] The presence of carboxylic and nitrile groups was supposed to facilitate the interaction between polymer, graphene oxide, zinc oxide, and ionic liquid. Authors claimed that ionic liquids were taking an active role in the healing mechanism by rearrangement of the ionic clusters of the zinc–carboxylate along with ionic liquid. Finally, they achieved a tensile strength of the composites of ca. 6.1 MPa, with a healing efficiency of 85% at the end.[60]

Aside from NBR, ENR is another commercial rubber that can be used for the metal-ligand coordination mechanism. ENR has highly reactive epoxide groups that not only can engage in metal ion coordination, but also have a wide range of reactivity towards various chemical reagents.[61–64] Modification of these epoxide groups enable ENR as a self-healing rubber. Considerable recent work has been done centralizing ENR.[35] In the ENR system, a microcapsule was produced at the molecular level through the coordination interaction between the Fe^{3+} metal ion and a complexing agent called 2,6-diaminopyridine. It was shown that the controlled release of these metal ion crosslinkers from the metal ion coordination complex provides self-healing properties. Finally, a tensile strength of ca. 3 MPa and an elongation at break of ca. 700%, with a healing efficiency of 60%, were achieved in this ENR system.[35]

Importantly, a very weakly crosslinked elastomer can provide self-healing–like properties due to the viscous flow of the raw polymer. In most reports, the mechanical properties are described as poor due to extremely low crosslinking density. However, higher mechanical properties, such as tensile strength and modulus at a given extension, are very important parameters for the application

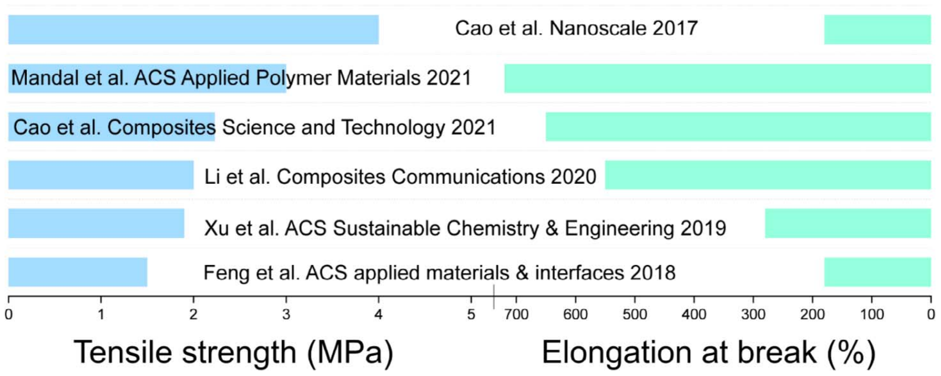

FIG. 4. — Comparison of mechanical properties (tensile strength and elongation at break) for the recently published ENR-based literature.

of self-healing rubber in various rubber products. Thus, a comparison is made here that focuses on the tensile strength and elongation at break of some studies in the field of elastomers (Figure 4). This comparison is mainly carried out with the self-healing ENR system. As for the mechanical data, the elongation at break is satisfactory, but the tensile strength values are lower than those of industrially relevant rubbers. The final mechanical properties can be improved further to a certain extent by adding conventional fillers (carbon black and silica). The question arises whether the principle of reversible network still works in the presence of conventional rubber fillers.[35,65–69]

IONIC CLUSTERS FORMATION IN SOFT ELASTOMER MATRIX

Ionic group or ionic cluster formation in the elastomeric matrix is one of the most appealing ways for the development of self-healing elastomers.[30,70–73] Das et al. published a report on the ionic cluster formation in elastomers and the development of self-healing rubbers. According to their study the reversibility of the ionic association enables self-healing processes by external stimuli such as temperature, and it is found that the mechanical properties of this kind of sample were superior to sulfur-cured elastomers. In this work, bromobutyl rubber (BIIR) was mixed and cured with butyl imidazole. Under thermal treatment, the butyl imidazole group was transformed into imidazolium salt with bromide as counterions and remained as pendant ionic groups in the BIIR chain. These ionic parts are allowed to form reversible ionic clusters that are responsible for self-healing character. The tensile strength and elongation at break were found to be ca. 9 MPa and 1000%, respectively, without the addition of any filler.[30]

Following the same principle, the study was further extended by using different imidazoles with variable side-chain lengths and the effect of the chain length was investigated. The effect of chain length on self-healing behavior was assessed for 1-methylimidazole, 1-butylimidazole, 1-hexylimidazole, 1-nonylimidazole, and 1(6-chlorohexyl)-1*H*-imidazole, for example, when mixed with BIIR. Distinct differences were observed in the final mechanical properties of the elastomers by using the different imidazoles. Shorter substituents in ionic groups, such as methyl imidazole, formed more compacted ionic aggregates, resulting in high mechanical properties (∼20 MPa) in the elastomer. However, stronger interactions within the ionic groups also inhibited rearrangements of the ionic clusters, resulting in a deterioration of self-healing ability. By contrast, long-chain imidazoles, such as nonyl imidazole, might have a steric hindrance associated with them. As a result, they inhibit ionic interactions inside the clusters, which has a positive impact on the elastomer's healing behavior. Nevertheless, at the same time, the long-chain imidazoles reduced the ultimate mechanical performance of the material.[31] Finally, imidazoles with a medium chain length, such as butyl or hexyl imidazole, offered a good balance between mechanical properties of the elastomer and self-healing efficiency. Using 1-hexylimidazole, the tensile strength and elongation at break were found to be ca. 12 MPa and 1100%, respectively, with a self-healing efficiency of 90%.

Besides BIIR, ionic clusters can also be formed in other functionalized rubbers such as ENR. 1*H*-Imidazole, because of having reactive 1 and 3 nitrogens, can react with the oxirane ring of ENR at a higher temperature, leading to crosslinking and formation of ionic species such as imidazolium cation and alkoxide counteranion. These ionic species could further facilitate ionic association, resulting in self-healing and reprocessing characteristics of the material. Tensile properties of 4.5 MPa, elongation at break of 700%, and a self-healing efficiency of 90% were attained in that study.[32]

CLICK CHEMISTRY: DIELS–ALDER AND DISULFIDE METATHESIS

Among many principles of self-healing rubber, Diels–Alder reaction and disulfide metathesis are the two key concepts of self-healing. Both belong to the category of reversible covalent bonding. Diels–Alder reaction is basically a reaction between the conjugated diene and another dienophile (substituted alkene).[74] Not all but some Diels–Alder reactions are reversible and can be reverted to their initial phase, which is called retro-Diels–Alder reaction, and this reversible concept is used in the preparation of self-healing materials. The concept of disulfide metathesis, however, is totally different. The reaction occurred by the nucleophilic attack in the disulfide linkage by a thiol group, resulting in an exchange of bonds between disulfide-containing moieties.[75] In this reaction, disulfide groups are split by a reduction reaction and regeneration of the bonds facilitated by the oxidation reaction. Naturally, the conventional disulfide metathesis reaction requires complex chemical operations involving reducing agents and bases.[76] These processes, however, are not feasible in an elastomer matrix because the dynamic exchange of disulfide bonds is difficult in the solid state of the material.[7] Consequently, the quest for a more practical procedure for this type of metathesis reaction is being undertaken, and recent advancements have revealed that it is possible to carry out disulfide metathesis by using simple UV radiation.[77,78]

The approaches may be implemented through synthesizing functionalized elastomers, e.g., polyurethane (PU) with the disulfide–furan functionality, or they could be implemented through the use of a commercial elastomer such as XNBR and subsequent functionalization. A PU elastomer was synthesized using polycaprolactone diol and 4,4′-methylenebis(phenyl isocyanate) followed by a reaction with a chain extender synthesized from 4-aminophenyl disulfide (APDS) and furfuryl glycidyl ether.[5] Therefore, the disulfide linkage as well as the conjugated dienes in the furan moieties were present in the structure of the PU elastomer. Finally, the Diels–Alder reaction was used to crosslink the two PU chains, which was accomplished by reacting the furan moieties with bismaleimide. In this way, the final elastomer actually was able to perform the Diels–Alder and retro-Diels–Alder reactions both. In addition, they could rearrange the bonds by a disulfide metathesis reaction. However, as previously stated, the cyclized and the non-cyclized component transformation must be controlled by different temperature conditions. The cyclized product could be generated at temperatures as low as 60 °C; however, for the reverse reaction to take place, temperatures as high as 100 °C were required.[5] Finally, despite a difficult synthesis, high tensile strength of 40 MPa and elongation at break of 450% were achieved. Because the synthesis of PU elastomers was complicated, researchers sought more reliable procedures that would allow them to use the Diels–Alder reaction in a commercial elastomer. A potential alternative was found in the case of XNBR, wherein the further functionalization of this rubber was described (Figure 5).[4] The –NH_2 group of furfuryl amine was found to be reactive

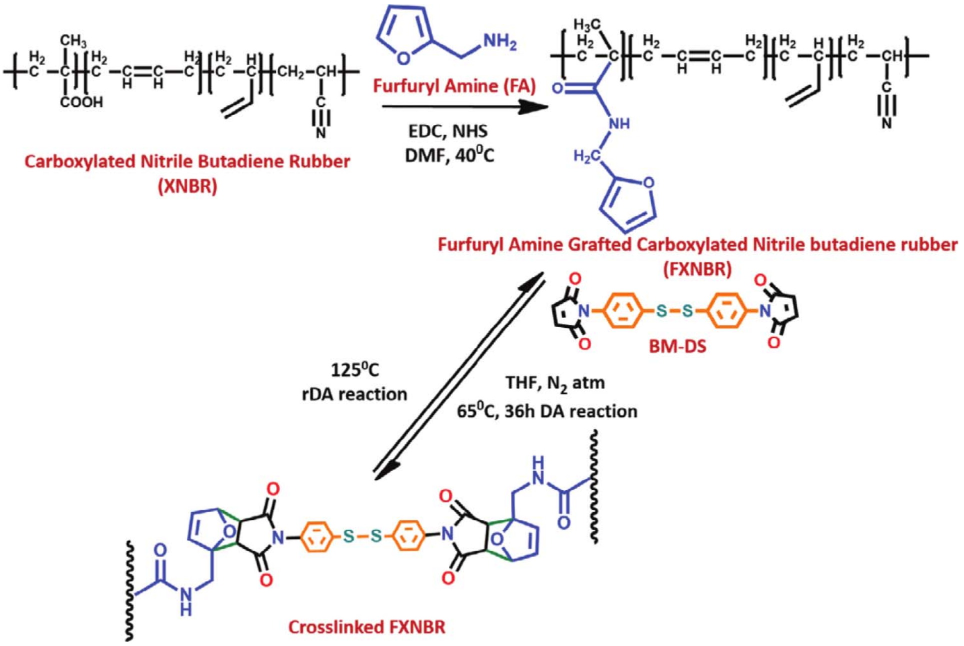

FIG. 5. — Diels–Alder and disulfide metathesis reaction between furfuryl amine–grafted XNBR and BM-DS (reproduced with permission from ref 4, Copyright 2021 Wiley).

toward the –COOH group of XNBR. Thus, a successful reaction was carried out between them, resulting in the formation of furfuryl amine–grafted XNBR (FXNBR). After this functionalization, the XNBR was able to participate in the Diels–Alder reaction through the pendent furan group as the conjugated diene and bismaleimide acted as a dienophile. Moreover, the crosslinker that reacts with the furan group was synthesized by the reaction between 1,1-(methylenedi-4,1-phenylene)bismaleimide (BM) and APDS. The additional advantage of this synthesis was that the crosslinked FXNBR now could execute dual regeneration of bonds: specifically, UV-triggered disulfide metathesis reaction and thermo-reversible Diels–Alder reaction. Subsequently, in this dual reversible network, a tensile strength of ca. 10 MPa, elongation at break of 1300%, and 88% self-healing efficiency were achieved. Notably, the roles of Diels–Alder and disulfide metathesis, in this case, were very different. In the heated condition, retro-Diels–Alder reaction was taking place, whereas in the cooling condition, the bonds were rearranged by the Diels–Alder reaction. By contrast, if the sulfur bonds were cleaved, it was again reformed by the disulfide metathesis reaction with the application of UV radiation.[4]

TETRAZINE CLICK REACTION

Metal ion coordination, for example, can take place in a functionalized elastomer backbone such as ENR, PDMS, poly(ethylene glycol), and polyacrylate. Diels–Alder reaction, in contrast, can occur with a conjugated diene and a substituted alkene. Hence, combining these two concepts in a single elastomer was not very straightforward. As a result, research has been done to integrate the two concepts into a single elastomeric matrix. The main objective of such research was to find a ligand that can react with the elastomer through the Diels–Alder process and coordinate with metal ions via functional groups. A ligand with this kind of ability is 3,6-di(2-pyridyl)-1,2,4,5-tetrazine (DPT), and the associated reaction with the unsaturated elastomer backbone was named

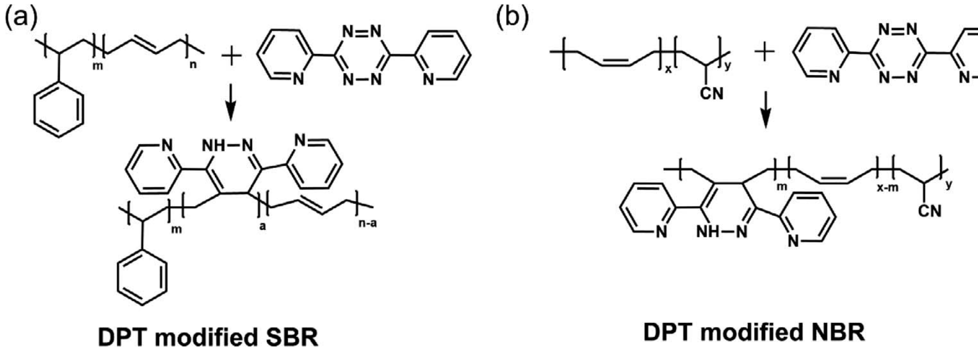

FIG. 6. — DPT-modified diene rubbers: (a) SBR (reproduced with permission from ref 55, Copyright 2021 American Chemical Society) and (b) NBR (reproduced with permission from and ref 54, Copyright 2021 Elsevier).

as tetrazine click reaction. This click reaction is the inverse electron–demanding Diels–Alder reaction (DA_{INV}), which is the interaction between an electron-rich dienophile and an electron-poor diene.

In this reaction, three π-bonds are converted to a pair of α-bonds and a new π-bond.[79–81] The application of DA_{INV} reactions with the commercial unsaturated SBR and di-pyridyl tetrazine was first reported by Wang et al.[55] A successful functionalization reaction took place between electron-withdrawing 3,6-substituent tetrazine and electron-donating dienophile (Figure 6a). Cu^{2+} metal ions were further added in the mixture, and multi-coordination took place between the nitrogen groups of tetrazine and the metal ions, resulting in good mechanical properties with recyclable abilities of the materials. However, self-healing behavior of the final coordinated materials was not reported.[55] The study was subsequently improved by using another unsaturated and functionalized rubber, NBR, by using two different types of metal ions: Zn^{2+} and Co^{2+}. The advantage of not using SBR but instead NBR was the additional nitrile group, which can function as an extra ligand in metal ion coordination reactions, such as (–CN-Zn-NC–) or (–CN-Co-NC–). The initial DA_{INV} reaction was carried out with the unsaturation of the elastomer and 3,6-substituent 1,2,4,5-tetrazine (Figure 6b). As the fully functionalized NBR was developed, metal ions were incorporated into the mixture to form multi-coordination bonds. As a result, high tensile strengths of 40 and 25 MPa, before and after healing, respectively, with a 200% elongation at break were achieved, which is superior to the normal metal ion–coordinated elastomers.[54] The tetrazine click concept could be a very fascinating aspect for future self-healing studies. The metal ion coordination–based self-healing system requires polar functionalized rubbers, such as ENR, PDMS, poly(ethylene glycol), and polyacrylate. Because most commercial elastomers, e.g., NR, BR, SBR, and NBR, possess unsaturation, in principle, all of these commercial unsaturated rubbers can have the ability to undergo DA_{INV} reaction that could result in a metal-coordinated crosslinked elastomer. Moreover, different types of tetrazine derivatives can be used to react with the elastomer to fulfill selective applications.

SCHIFF-BASE CHEMISTRY

Schiff-bases are formed by nucleophilic addition reaction of an aliphatic or aromatic amine and a carbonyl compound, resulting in a hemiaminal or carbinolamine ($–C(OH)(NR_2)–$) linkage, followed by an imine or azomethine ($R–CH{=}NR'$, $R' \neq H$) formation by the elimination of water molecules.[82,83] Schiff-base bonds are the derivatives of aldehydes or ketones and a subclass of

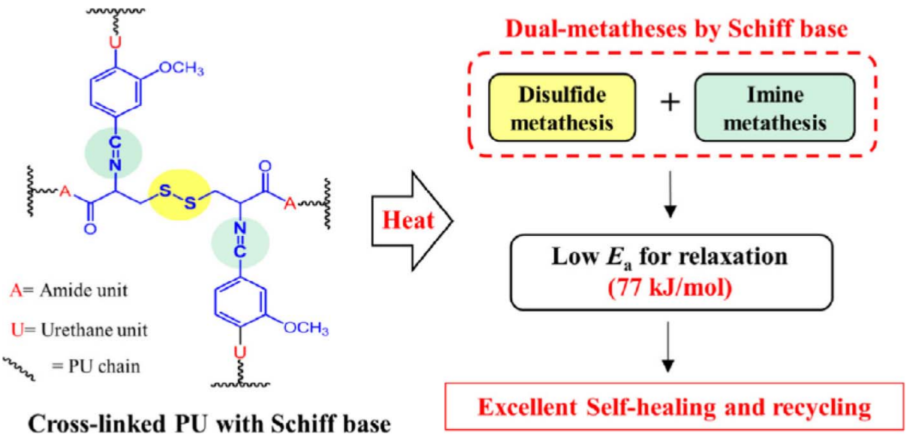

FIG. 7. — PU is crosslinked by Schiff-base containing a disulfide linkage (reproduced with permission from ref 41, Copyright 2019 Elsevier).

imine bonds. Under moderate conditions, they are one of the most fundamental dynamic covalent bonds.

Cystine and vanillin are the two renewable biomaterials that have the capability to form a dual-dynamic imine bond. Cystine also has a disulfide bond in its structure that can participate in the disulfide metathesis reaction and contribute to the dynamic networking behavior of the final material. Recently, a few self-healing studies have been carried out centralizing crosslinked PU elastomer.[84,85] However, Schiff-base PU elastomers (SPUs) showed a remarkable improvement in the case of self-healing and recyclability due to the synergistic effect of imine metathesis and other types of supporting dynamic covalent bonding. In a recent report by Lee et al., a dual responsive self-healing behavior was shown in SPU elastomer with the effect of temperature and UV radiation.[41] In addition, the final material was re-processable for several cycles (Figure 7). Further improvement was made with the careful selection of PU elastomers. The phase locking of the imine metathesis reaction in the PU elastomer and the ratio of a hard crystalline segment to the soft segment of PU significantly control the final mechanical property and self-healing behavior of the material. Choosing the diisocyanate part incorrectly in the preparation of PU elastomer could result in an amorphous, sticky, and transparent PU elastomer that would compromise the material's final mechanical and self-healing properties, i.e., unsymmetrical toluene diisocyanate and isophorone diisocyanate (IPDI). A highly symmetrical and crystalline PU elastomer made from highly symmetrical hexamethylene diisocyanate, in contrast, had the opposite impact on self-healing due to the crystallinity obstructing full contact of the damaged parts. In addition, the self-healing required a high-temperature condition because of the crystalline part's high melting point. However, the optimization was done in a recent report by Hu et al.[86], and it was demonstrated that dicyclohexylmethane 4,4′-diisocyanate had the potential to form a robust PU elastomer with a balance of both mechanical and self-healing properties. In this report, the self-healing mechanism was demonstrated in two parts. First, microphase separation was facilitated by the double bond of imine and the chain segments were organized during strain-induced crystallization. Second, the dynamic imine exchange reaction was phase locked in the hard phases of PU elastomer. As the temperature increased, the self-healing was accelerated by the rapid relaxation of the hard phases. Finally, tensile strength of 40 MPa and elongation at break of 850%, with a very high self-healing efficiency of 96%, were achieved.[86]

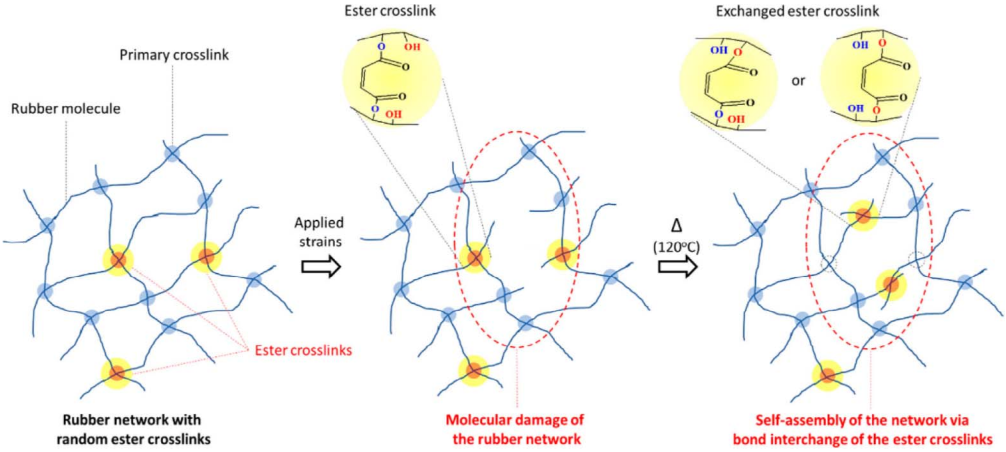

FIG. 8. — Transesterification reaction, exchange of ester crosslinks in elastomer matrix after damage (reproduced from ref 47, MDPI Creative Commons CC BY 4.0 license).

ANHYDRIDE, DICARBOXYLIC ACID CURING, AND TRANSESTERIFICATION

The role of metal ion coordination in ENR has already been addressed in this article; nonetheless, as previously stated, the epoxy group of ENR is so reactive that it can participate in a variety of chemical reactions.

A report by Pire et al. demonstrated for the first time that dicarboxylic acids had a potential to crosslink the ENR-originating β-hydroxy-ester groups in the elastomeric chain.[87] However, this curing reaction has a major disadvantage in that the crosslinking between ENR and dicarboxylic acids required high temperatures and extended curing times, which had a negative impact on the cured rubber's final mechanical properties. They solved the problem by using a suitable catalyst, a substituted imidazole (1,2-dimethylimidazole), that accelerated the reaction between dicarboxylic acids and the epoxy ring of ENR.[88]

Along with the dicarboxylic acid, another important concept in the study of self-healing was transesterification. Transesterification is basically a process of exchanging the alkyl group of an ester (R'') with the alkyl group of an alcohol (R'), making the bond dynamic and reversible. Recently, considerable research has been carried out using these two concepts. Hydrolyzed maleic anhydride, which has two carboxyl groups, is used to cure the ENR by opening its oxirane ring. As a result, ester crosslinking takes place and hydroxyl groups are formed in the elastomer matrix. Moreover, a transesterification catalyst, zinc acetate dihydrate [$Zn\ (CH_3COO)_2 \cdot 2H_2O$] was added and the system was named the EMZ (for ENR–maleic anhydride–ZnAc) by Algaily et al.[47] (Figure 8). Because of this catalyst, thermodynamically transferable ester bonding can interchange and reform the bonds at an elevated temperature (120 °C) and could heal the molecular scale defects through the transesterification reaction. The entire EMZ system was incorporated in a blend with NR, a sulfur-vulcanizing system, and fillers to achieve good tensile strength (15 MPa) and elongation at break (600%)[47]; however, a clear understanding of the reversible network cannot be realized due to the presence of many complicated chemical substances in the rubber systems. The effect of the esterification catalyst, for example, zinc acetate dihydrate, was not restricted to ENR, but it could be applied in another thermoset system such as polybenzoxazine. In this system, it was demonstrated that the transesterification reaction followed the first order kinetics and its thermoset was found to perform self-healing behavior quite efficiently, which was realized by multiple damage and recovery cycle experiments.[89] Despite the fact that the study was carried out in this

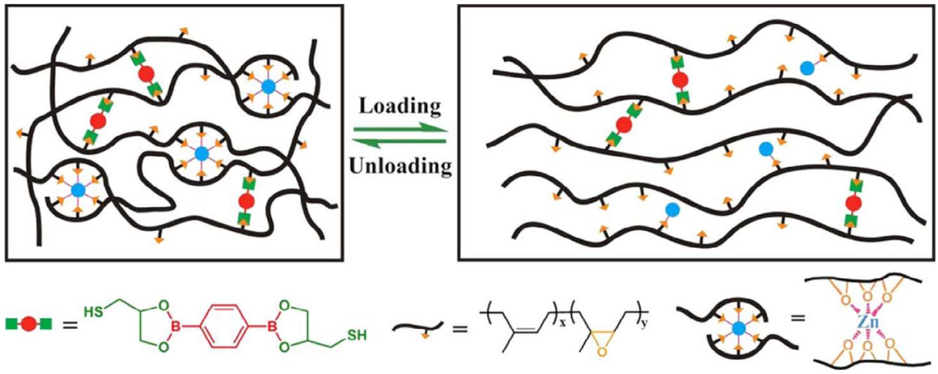

FIG. 9. — Reversibility of boronic ester crosslinks as ENR is reacted with boronic ester crosslinker carrying dithiol group (reproduced with permission from ref 92, Copyright 2019 American Chemical Society).

synthetic resin, the concept of transesterification remained exactly the same as described in other literature.[47]

BORONIC ESTER CROSSLINKING

A boronic acid is a chemical similar to orthoboric acid [$B(OH)_3$]; however, one hydroxyl group is substituted by an alkyl or aryl group.[90] It has the characteristics of a Lewis acid and is classified as an organoborane. Boronic acid is reported to have low intrinsic toxicity and thus is used in the production of pharmaceutical drugs from Suzuki coupling reaction to sustainable elastomer development.[91] Boronic esters are formed when a boronic acid reacts with an alcohol, and their distinguishing property is the ability to form dynamic covalent compounds. In recent self-healing literature, it can be seen that boronic ester crosslinking principle is also used to prepare and develop self-healing rubbers. However, the crosslinking or grafting of boronic esters in the elastomer backbone is not straightforward. Synthesis of different boronic ester derivatives is needed to react with some functionalized rubber. A dithiol boronic ester BDB [2,2′-(1,4-phenylene)-bis(4-mercaptan-1,3,2-dioxaborolane)] was synthesized that in turn could react with the epoxy group of ENR with the assistance of the catalyst 4-dimethylaminopyridine. Transesterification was the key mechanism here for the dynamic behavior of the covalent bonding; however, to achieve better mechanical properties, the matrix was further crosslinked by metal ion coordination, which was a non-covalent interaction (Figure 9). In addition to boronic ester crosslinking, $ZnCl_2$ was also further added in the ENR system to allow epoxy groups to participate in coordination bonds with zinc ions. This coordination bond was explained as a sacrificial reversible linkage that is responsible for the self-healing behavior. With the application of both dynamic covalent (boronic ester) and non-covalent (coordination) interactions, finally, a tensile strength of 9 MPa and elongation at break of ca. 650% was achieved in the study.[92]

Another thorough investigation based on boronic ester linkages was conducted with PU elastomers. In this study, PU was prepared via the reaction between a polyester diol and IPDI. The mechanism was predominantly boric acid ionization in the alkaline atmosphere and the production of boronic ester linkages in the matrix. The self-recovery of the material followed a damage event that took place after exposing the material to a certain temperature that triggered the boric acid transformation. Eventually, free boric acids were generated, resulting in the formation of new crosslinking bridges in the matrix. In addition to boric acid, another chain extender named 4,4-diaminodiphenyl disulfide was added to the reaction mixture and it was capable rearranging the damaged part with disulfide metathesis reactions. Finally, 27 MPa of tensile strength and 1200% elongation at break were achieved in this study.[51]

DYNAMIC HYDROGEN BONDING

Hydrogen bonding is characterized by the electrostatic interaction that exists between an electropositive hydrogen atom and another electronegative atom that carries a lone pair of electrons.[93] It is well established that hydrogen bonds are thermo-reversible and are capable of acting as dynamic healing elements. Because hydrogen bonds are weaker than covalent bonds, only hydrogen bonds may not always impart good mechanical properties in a material; however, they are considered as a good supportive role in a combination self-healing. The term "combination self-healing" is applied when two or more self-healing mechanisms are incorporated into a single self-healing matrix. If ENR is considered as a self-healing matrix, in most of the cases, hydroxyl groups are formed by the opening of the oxirane rings. As a result, hydrogen bonds could be formed and can actively participate in the self-healing event. Because the oxirane ring of ENR has a high affinity toward the amine and carboxylic groups, a careful selection of chemical reagents containing these chemical functionalities can fulfill the aforementioned reactions effectively. For example, in recent work, dithiodibenzoic acid and dithiodianiline are allowed to react with ENR.[94] The main target of the study was to incorporate disulfide groups in the elastomer matrix and to activate disulfide metathesis after damage. Moreover, during the reaction, a significant quantity of hydroxyl groups was produced that can be involved in the self-healing mechanism. Finally, a tensile strength of 8 MPa and elongation at break of 400% were achieved as a result of this combination of two different self-healing principles.[94] It is also reported that in addition to chemical crosslinkers, reversible hydrogen bonds can be formed in the elastomer matrix by other rubber additives, such as fillers, e.g., cellulose. Three different types of cellulose can be used to obtain green self-healing materials: cellulose nanocrystals, cellulose nanofibers, and microcrystalline cellulose.[95] In addition, recent research from Cao et al. claimed when an ENR system loaded with tunicate cellulose nanocrystals, the system was shown to be able to form H-bond–based supramolecular elastomer matrix.[65] Essentially, the basic mechanism of self-healing, in this case, was relatively straightforward: hydroxyl groups in tunicate cellulose reacted with functional groups in elastomers, such as the oxirane ring of ENR, and reversible hydrogen bonds were formed in the reaction. The research was carried out by simply adding cellulose suspension in the ENR latex without any kind of surface modification. Finally, tensile strength of ca. 4 MPa and a self-healing efficiency of 86% were achieved in that study.

SUPRAMOLECULAR ZWITTERIONIC NETWORK FORMATION

So far, a vast range of non-covalent intrinsic self-healing mechanisms have been discussed. Most of the mechanisms fall under the category of a supramolecular network and include hydrogen bonding, metal ion coordination, and ionic cluster formation. A supramolecular network is concerned with the chemistry of molecular assemblies that are stabilized by intermolecular attractions. Superior to dynamic covalent bonding, supramolecular interactions have the following advantages of increased sensitivity, lower activation energy, wider range of architectural selection, and faster response to attain the equilibrium state.[96] Moreover, the reversibility of these interactions predominantly depends on the rate constants of association and dissociation of the molecular assemblies. Achievement of higher crosslinking density would be rather limited with this supramolecular network. This can be attained by dynamic covalent network. The supramolecular networks also include zwitterionic complexes. Zwitterions or dipolar ions are small molecules containing an equal number of cationic and anionic functional groups in the same structure with an

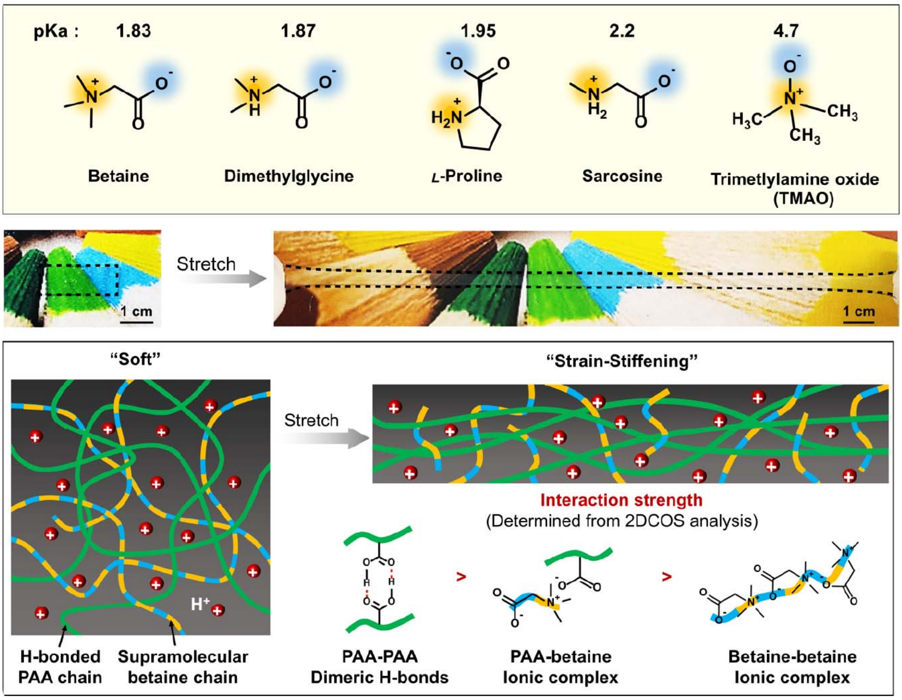

FIG. 10. — Chemical structures of different types of zwitterions and the formation of ionic complexes and hydrogen bonds (reproduced from ref 38, MDPI Creative Commons CC BY 4.0 license).

overall neutral charge.[97] The intermolecular force of attraction in zwitterions is extremely weak and allows them to be fragmented when stretched while also undergoing rapid entropy-driven recombination, resulting in a self-recoverable system. Recently, an extensive study was reported revealing the effect of various zwitterions in the self-healing behavior of polymers.[38] Fundamentally, five zwitterions were selected for this study to analyze their influence on the self-healing system (Figure 10). These zwitterions were betaine, dimethylglycine, L-proline, sarcosine, and trimethylamine oxide. They were involved in the polymerization process of AA. As a result, three types of bonds were generated: COOH dimeric H-bonds, polymer–zwitterion complex, and zwitterion–zwitterion complex. A greater outcome was observed in the case of polyacrylic acid (PAA)–betaine complex. In this case, the covalent PAA chains were self-crosslinked by strong dimeric H-bonds and the other supramolecular betaine chains were formed by ionic complexes. Furthermore, the covalent bond provided mechanical strength, whereas the other supramolecular betaine complexes assisted in self-healing through their ability to reorganize themselves as a result of entropy-driven rearrangement.[38]

MECHANOCHEMICAL GENERATION OF REACTIVE MOLECULAR SPECIES AND RADICAL COUPLING

Mechanochemistry is a simple and straightforward way of designing self-healing materials that activates the healing processes by the damage event itself.[2] In mechanochemistry, an in situ stimulation of mechanochemical materials results in the generation of radical species. In this process, for example, the rubber chain is cleaved, resulting in the formation of two free radicals that can subsequently combine if no additional radical-scavenging agents are present in damaged sites. In general, when the rubber chain is ruptured and reconstructed, it is called C–C homolysis and

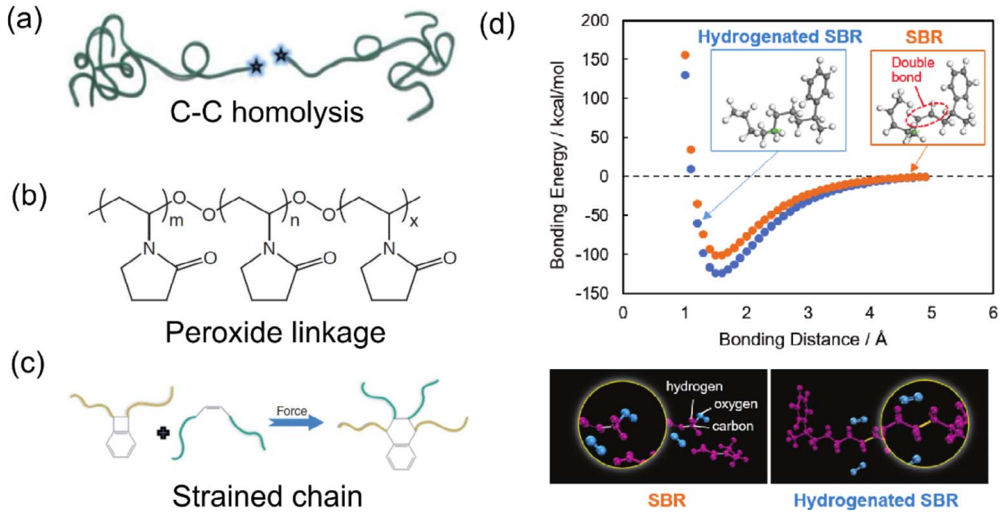

FIG. 11. — Different types of mechanochemical coupling: (a) C–C homolysis, (b) radical combination in peroxide-linked polymers, (c) coupling in a strained chain (reproduced with permission from ref 2, Copyright 2013 Wiley), and (d) radical coupling in H-SBR.

radical coupling (Figure 11a). However, it is not straightforward because oxygen or some other species in the environment generally stabilizes those radicals. A study of the molecular structures of SBR and hydrogenated SBR (H-SBR) was recently conducted, and their differences in wear behavior were reported. The quantum chemical calculation results revealed the existence of weaker bonds in SBR because of the allylic resonance of the double bond, whereas the bonds in H-SBR rubber were stronger and more resistant to mechanically induced chain scission. However, the interesting finding was the comparison of radical stability and the mechanochemical reaction sensitivity between the two rubbers. According to the findings, cleavage of SBR bonds produced more stable free radicals than H-SBR, which could react with the oxygen molecules due to their extended lifetime. The lifetime of free radicals for the H-SBR, in contrast, is too short to interact with oxygen molecules, and the H-SBR instantly bonds with the opposite end of a free radical. As a result of the increased sensitivity of H-SBR radicals, recombination could occur almost instantaneously (Figure 11d).[98] Nevertheless, mechanochemistry has progressed in a more advanced manner, and it is now possible to embed certain mechanophores in the elastomer matrix, which does not require the use of any protective chemicals or encapsulation to allow for the self-recombining of the mechanophores.[99,100] So, alternative polymers with easily cleavable linkages were developed that were either peroxide-linked (Figure 11b) or azo-linked polymers, such as poly(vinylpyrrolidone)[101] or azo-functionalized poly(ethylene glycol),[102] respectively. Some polymers are designed with strained rings that can transform into a simpler structure after an external impact, and the material can be healed by opening the strained ring (Figure 11c). Because of the sensitivity and directional nature of mechanochemistry when a polymer is exposed to an external impact, the mechanical force is oriented in such a manner that it reaches the mechanoresponsive groups and ruptures the weakest reversible bond in the polymer matrix.

SUMMARY AND CONCLUSION

There are some other well-known material properties that have similar characteristics, but should not be confused with the concept of self-healing, such as stickiness and tackiness. To apply the concept of self-healing elastomers, a three-dimensional crosslinking network must be formed in the material system, otherwise the dimensional stability of the system will be lost.[30] Various studies have used the viscous properties of materials and tried to find the self-healing effect of the material, which is in the nature of a viscous or semi-solid fluid. Despite many publications, the application of such materials for commercial purposes is still far away. In addition, the difference in network structure may have an effect on the relaxation behavior of the self-healing materials. The self-healing network structure usually consists of a weak network so that the weak bonds are working as a sacrifice network to protect the main network structure from unrecoverable damage. Inevitably, most self-healing materials would tend to undergo creep and permanent set behavior. There is a conflict between self-healing character and bond strength. In general, reversible sacrificing bonds can be realized by weak bonds being essential for self-healing materials, compensating with stable and strong bonds. This is the reason why creep behavior is a concern for self-healing materials. However, creep is observed only if the applied load is higher than a threshold. From the practical point of view, the balance between increasing threshold and self-healability is a significant issue. It is therefore required to carry out standard creep tests to gain an understanding of the network behavior to serve application requirements. So far, fracture mechanical behavior, especially at application-oriented cyclic-dynamic conditions, was not in the focus of research, although it is of the highest importance for technically relevant rubbery materials. The formation and growth of (sub)-microscopic defects (i.e., cavitation), mainly originating from failure events at the nano- or molecular scale, have a huge impact on macroscopic damage events.[103–107] Here, the self-healing capacities are expected to exhibit high potential for innovative material concepts. In addition, some recent studies have shown that a large number of chemical reagents are used to develop self-healing rubbers. There still remain many unclear points to be tackled. In an editorial, an explanation was given as "The self-healing process involves one component only, even in multi-component systems. The repairing of damaged materials as a result of chemical reactions between two or more components is 'chemically assisted healing' but not 'self-healing'."[108] Finally, because self-healing is a biological term, it is necessary to quantify this character by a proper scientific method. Likely, there has been nearly no approach or concept in this regard, and this is one of the most challenging tasks for a material scientist. Regardless, the development of self-healing materials, specifically in rubber systems, is still in the proof-of-concept phase and "academic" in character. Much more research and effort are needed to realize the concept in real application.

ACKNOWLEDGEMENTS

A.D. acknowledges Deutsche Forschungsgemeinschaft (DFG; German Research Foundation) project 404941515 under SPP2100 Programme for partial financial support. G.H. and S.W. acknowledge DFG project 380321452/GRK2430 for financial support.

REFERENCES

[1] *Self-healing Materials: Fundamentals, Design strategies, and Applications*, S. K. Ghosh, Ed., WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2009.

[2] *Self-Healing Polymers: From Principles to Applications*, W. H. Binder, Ed., Wiley-VCH Verlag GmbH, Weinheim, Germany, 2013.

[3] S. Utrera-Barrios, R. Verdejo, M. A. López-Manchado, and M. H. Santana, *Mater. Horiz.* **7**, 2882 (2020).

[4] S. Sarkar, S. L. Banerjee, and N. K. Singha, *Macromol. Mater. Eng.* **306**, 2000626 (2021).

[5] P. K. Behera, S. K. Raut, P. Mondal, S. Sarkar, and N. K. Singha, *ACS Appl. Polym. Mater.* **3**, 847 (2021).

[6] Y. Eom, S. M. Kim, M. Lee, H. Jeon, J. Park, E. S. Lee, S. Y. Hwang, J. Park, and D. X. Oh, *Nat. Commun.* **12**, 1 (2021).

[7]A. Das, H. H. Le, J. Vuorinen, and G. Heinrich, *ACS Appl. Mater. Interfaces* **9**, 14547 (2017).

[8]T. J. Deming, *Curr. Opin. Chem. Biol*. **3**, 100 (1999).

[9]A. Reinecke, L. Bertinetti, P. Fratzl, and M. J. Harrington, *J. Struct. Biol*. **196**, 329 (2016).

[10]Y. Miwa, J. Kurachi, Y. Sugino, T. Udagawa, and S. Kutsumizu, *Soft Matter* **16**, 3384 (2020).

[11]P. G. De Gennes, *Chem. Phys*. **55**, 572 (1971).

[12]A. Y. Grosberg and A. R. Khokhlov, *Giant Molecules: Here, There, and Everywhere*, 2nd ed., World Scientific, Singapore, 2010.

[13]Y. Yang and M. W. Urban, "Thermodynamics of Self-Healing in Polymeric Materials," in *RSC Polymer Chemistry Series No. 5, Healable Polymer Systems*, W. Hayes and B. W Greenland, Eds., The Royal Society of Chemistry, London, 2013, p. 126.

[14]K. Yu, A. Xin, and Q. Wang, *J. Mech. Phys. Solids* **121**, 409 (2018).

[15]M. J. Mateyisi, J. U. Sommer, K. K. Müller-Nedebock, and G. Heinrich, *Chem. Phys*. **148**, 244901 (2018).

[16]M. Doi, *Soft Matter Physics*, Oxford University Press, London, 2013.

[17]B. J. Blaiszik, S. L. Kramer, S. C. Olugebefola, J. S. Moore, N. R. Sottos, and S. R. White, *Annu. Rev. Mater. Res*. **40**, 179 (2010).

[18]S. R. White, B. J. Blaiszik, S. L. Kramer, S. C. Olugebefola, J. S. Moore, and N. R. Sottos, *Am. Sci*. **99**, 392 (2011).

[19]Z. Yin, J. Guo, J. Qiao, and X. Chen, *Colloid Polym. Sci*. **298**, 67 (2020).

[20]J. Yang, M. W. Keller, J. S. Moore, S. R. White, and N. R. Sottos, *Macromolecules* **41**, 9650 (2008).

[21]M. W. Lee, S. S. Yoon, and A. L. Yarin, *ACS Appl. Mater. Interfaces* **9**, 17449 (2017).

[22]I. S. Vintila, J. Ghitman, H. Iovu, A. Paraschiv, A. Cucuruz, D. Mihai, and I. F. Popa, *Polymers* **14**, 2798 (2022).

[23]M. W. Urban, D. Davydovich, Y. Yang, T. Demir, Y. Zhang, and L. Casabianca, *Science* **362**, 220 (2018).

[24]J. Chen, F. Li, Y. Luo, Y. Shi, X. Ma, M. Zhang, D. Boukhvalov, and Z. Luo, *J. Mater. Chem*. **A7**, 15207 (2019).

[25]S. Burattini, B. W. Greenland, D. H. Merino, W. Weng, J. Seppala, H. M. Colquhoun, W. Hayes, M. E. Mackay, I. W. Hamley, and S. J. Rowan, *J. Am. Chem. Soc*. **132**, 12051 (2010).

[26]L. Zhang, H. Wang, Y. Zhu, H. Xiong, Q. Wu, S. Gu, X. Liu, G. Huang, J. Wu, *ACS Appl. Mater. Interfaces* **12**, 53239 (2020).

[27]D. Davydovich and M. W. Urban, *Nat. Commun*. **11**, 1 (2020).

[28]Y. Cao, H. Wu, S. I. Allec, B. M. Wong, D. S. Nguyen, and C. Wang, *Adv. Mater*. **30**, 1804602 (2018).

[29]Z. Xie, B. L. Hu, R. W. Li, and Q. Zhang, *ACS Omega* **6**, 9319 (2021).

[30]A. Das, A. Sallat, F. Böhme, M. Suckow, D. Basu, S. Wießner, K. W. Stöckelhuber, B. Voit, and G. Heinrich, *ACS Appl. Mater. Interfaces* **7**, 20623 (2015).

[31]M. Suckow, A. Mordvinkin, M. Roy, N. K. Singha, G. Heinrich, B. Voit, K. Saalwächter, and F. Böhme, *Macromolecules* **51**, 468 (2017).

[32]S. Mandal, S. Hait, F. Simon, A. Ghosh, U. Scheler, I. Arief, T. Tada, T. X. Hoang, S. Wießner, G. Heinrich, and A. Das, *ACS Appl. Polym. Mater*. **4**, 6612 (2022).

[33]J. Liu, C. S. Y. Tan, Z. Yu, N. Li, C. Abell, and O. A. Scherman, *Adv. Mater*. **29**, 1605325 (2017).

[34]S. Nomimura, M. Osaki, J. Park, R. Ikura, Y. Takashima, H. Yamaguchi, and A. Harada, *Macromolecules* **52**, 2659 (2019).

[35]S. Mandal, F. Simon, S. S. Banerjee, L. B. Tunnicliffe, C. Nakason, C. Das, M. Das, K. Naskar, S. Wiessner, and G. Heinrich, *ACS Appl. Polym. Mater*. **3**, 1190 (2021).

[36]S. Wu, S. Fang, Z. Tang, F. Liu, and B. Guo, *Mater. Des*. **192**, 108756 (2020).

[37]X. An, J. Liu, J. H. Zhang, X. Huang, T. Zhu, H. Yan, X. Jia, and Q. Zhang, *Mater. Chem. Front*. **6**, 1779 (2022).

[38]W. Zhang, B. Wu, S. Sun, and P. Wu, *Nat. Commun*. **12**, 1 (2021).

[39]J. Kang, J. Kim, K. Choi, P. H. Hong, H. J. Park, K. Kim, Y. K. Kim, G. Moon, H. Jeon, and S. Lee, *Chem. Eng. J*. **420**, 127636 (2021).

[40] J. He, F. Song, X. Li, L. Chen, X. Gong, and W. Tu, *J. Polym. Res*. **28**, 1 (2021).

[41] S. H. Lee, S. R. Shin, and D. S. Lee, *Mater. Des*. **172**, 107774 (2019).

[42] C. Lu, C. Wang, J. Wang, Q. Yong, and F. Chu, *Chem. Eng. J*. **425**, 130652 (2021).

[43] D. Yilmaz, D. Lansade, S. Lewandowski, S. Perraud, A. Llevot, and S. Carlotti, *Mater. Today Chem*. **24**, 100860 (2022).

[44] S. Terryn, J. Brancart, E. Roels, R. Verhelle, A. Safaei, A. Cuvellier, B. Vanderborght, and G. Van Assche, *Macromolecules* **55**, 5497 (2022).

[45] W. Fan, Y. Jin, L. Shi, W. Du, R. Zhou, S. Lai, Y. Shen, and Y. Li, *ACS Appl. Mater. Interfaces* **12**, 6383 (2020).

[46] J. Liu, X. Ma, Y. Tong, and M. Lang, *Appl. Surf. Sci*. **455**, 318 (2018).

[47] B. Algaily, W. Kaewsakul, S. S. Sarkawi, and E. Kalkornsurapranee, *Polymers* **13**, 39 (2021).

[48] X. Yang, Y. Guo, X. Luo, N. Zheng, T. Ma, J. Tan, C. Li, Q. Zhang, J. Gu, *Compos. Sci. Technol*. **164**, 59 (2018).

[49] W. Fan, Y. Jin, L. Shi, W. Du, and R. Zhou, *Polymer* **190**, 122199 (2020).

[50] L. Lyu, D. Li, Y. Chen, Y. Tian, and J. Pei, *Constr. Build. Mater*. **293**, 123480 (2021).

[51] M. Xu, B. Cheng, Y. Sheng, J. Zhou, M. Wang, X. Jiang, and X. Lu, *ACS Appl. Polym. Mater*. **2**, 2228 (2020).

[52] K. Song, W. Ye, X. Gao, H. Fang, Y. Zhang, Q. Zhang, X. Li, S. Yang, H. Wei, and Y. Ding, *Mater. Horiz*. **8**, 216 (2021).

[53] Z. H. Zhao, D. P. Wang, J. L. Zuo, and C. H. Li, *ACS Mater. Lett*. **3**, 1328 (2021).

[54] Q. Wang, Y. Shi, Q. Li, and C. Wu, *Eur. Polym. J*. **150**, 110415 (2021).

[55] Q. Wang, W. Wang, Q. Li, and C. Wu, *Ind. Eng. Chem. Res*. **60**, 2163 (2021).

[56] S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. Sriram, E. N. Brown, and S. Viswanathan, *Nature* **409**, 794 (2001).

[57] S. Yu, H. Zuo, X. Xu, N. Ning, B. Yu, L. Zhang, and M. Tian, *ACS Appl. Polym. Mater*. **3**, 2667 (2021).

[58] C. H. Li, C. Wang, C. Keplinger, J. L. Zuo, L. Jin, Y. Sun, P. Zheng, and Y. Cao, *Nat. Chem*. **8**, 618 (2016).

[59] Q. Y. Yin, C. H. Dai, H. Chen, K. Gou, H. Z. Guan, P. H. Wang, J. T. Jiang, and G. S. Weng, *Chin. J. Polym. Sci*. **39**, 554 (2021).

[60] M. Das, T. Aswathy, S. Pal, and K. Naskar, *Eur. Polym. J*. **158**, 110691 (2021).

[61] K. Damampai, S. Pichaiyut, S. Mandal, S. Wießner, A. Das, and C. Nakason, *Polymers* **13**, 4145 (2021).

[62] K. Damampai, S. Pichaiyut, A. Das, and C. Nakason, *eXPRESS Polym. Lett*. **16**, 812 (2022).

[63] A. S. Hashim, S. Kohjiya, and Y. Ikeda, *Polym. Int*. **38**, 111 (1995).

[64] A. Hashim and S. Kohjiya, *J. Polym. Sci., Part A: Polym. Chem*. **32**, 1149 (1994).

[65] L. Cao, D. Yuan, C. Xu, and Y. Chen, *Nanoscale* **9**, 15696 (2017).

[66] L. Cao, Z. Gong, C. Liu, J. Fan, and Y. Chen, *Compos. Sci. Technol*. **207**, 108750 (2021).

[67] J. Li, P. Zhang, L. Chen, G. Li, H. Chen, C. Jia, Y. Wu, M. Chen, X. Zhao, and P. Song, *Compos. Commun*. **22**, 100530 (2020).

[68] C. Xu, J. Nie, W. Wu, Z. Zheng, and Y. Chen, *ACS Sustainable Chem. Eng*. **7**, 15778 (2019).

[69] Z. Feng, J. Hu, H. Zuo, N. Ning, L. Zhang, B. Yu, and M. Tian, *ACS Appl. Mater. Interfaces* **11**, 1469 (2018).

[70] H. Le, S. Hait, A. Das, S. Wiessner, K. Stoeckelhuber, F. Böhme, U. Reuter, K. Naskar, G. Heinrich, and H. Radusch, *eXPRESS Polym. Lett*. **11**, 230 (2017).

[71] H. H. Le, F. Böhme, A. Sallat, S. M. auf der LandwehrWießner, U. Reuter, K. W. Stöckelhuber, G. Heinrich, H. J. Radusch, and A. Das, *Macromol. Mater. Eng*. **302**, 1600385 (2017).

[72] A. Das, A. Sallat, F. Böhme, E. Sarlin, J. Vuorinen, N. Vennemann, G. Heinrich, and K. W. Stöckelhuber, *Polymers* **10**, 94 (2018).

[73] A. Sallat, A. Das, J. Schaber, U. Scheler, E. S. Bhagavatheswaran, K. W. Stöckelhuber, G. Heinrich, B. Voit, and F. Böhme, *RSC Adv*. **8**, 26793 (2018).

[74] M. C. Kloetzel, *Org. React*. **4**, 1 (1948).

[75] R. Singh and G. M. Whitesides, *J. Am. Chem. Soc*. **112**, 1190 (1990).

[76] R. Caraballo, M. Rahm, P. Vongvilai, T. Brinck, and O. Ramström, *Chem. Commun*. **48**, 6603 (2008).

[77] U. F. Fritze and M. von Delius, *Chem. Commun.* **52**, 6363 (2016).

[78] F. Denes, M. Pichowicz, G. Povie, and P. Renaud, *Chem. Rev.* **114**, 2587 (2014).

[79] D. Wang, W. Chen, Y. Zheng, C. Dai, K. Wang, and B. Ke, *Org. Biomol. Chem.* **12**, 3950 (2014).

[80] C. F. Hansell, A. Lu, J. P. Patterson, and R. K. O'Reilly, *Nanoscale* **6**, 4102 (2014).

[81] G. J. Bodwell, Z. Pi, and I. R. Pottie, *Synlett* **4**, 477 (1999).

[82] G. Moss, P. Smith, and D. Tavernier, *Pure Appl. Chem.* **67**, 1307 (1995).

[83] H. Schiff, *Justus Liebigs Ann. Chem.* **140**, 92 (1866).

[84] Z. P. Zhang, M. Z. Rong, and M. Q. Zhang, *Adv. Funct. Mater.* **28**, 1706050 (2018).

[85] V. Solouki Bonab, V. Karimkhani, and I. Manas-Zloczower, *Macromol. Mater. Eng.* **304**, 1800405 (2019).

[86] J. Hu, R. Mo, X. Sheng, and X. Zhang, *Polym. Chem.* **11**, 2585 (2020).

[87] M. Pire, S. Norvez, I. Iliopoulos, B. Le Rossignol, and L. Leibler, *Polymer* **51**, 5903 (2010).

[88] M. Pire, S. Norvez, I. Iliopoulos, B. Le Rossignol, and L. Leibler, *Polymer* **52**, 5243 (2011).

[89] F. Fu, M. Huang, W. Zhang, Y. Zhao, and X. Liu, *Sci. Rep.* **8**, 1 (2018).

[90] A. McNaught and A. Wilkinson, *IUPAC Compendium of Chemical Terminology*, 2nd ed., Blackwell Scientific Publications, Oxford, UK, 1997.

[91] A. J. Lennox and G. C. Lloyd-Jones, *Chem. Soc. Rev.* **43**, 412 (2014).

[92] Y. Chen, Z. Tang, Y. Liu, S. Wu, and B. Guo, *Macromolecules* **52**, 3805 (2019).

[93] E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, and P. Hobza, *Pure Appl. Chem.* **83**, 1637 (2011).

[94] B. Cheng, X. Lu, J. Zhou, R. Qin, and Y. Yang, *ACS Sustainable Chem. Eng.* **7**, 4443 (2019).

[95] K. Roy, A. Pongwisuthiruchte, S. C. Debnath, and P. Potiyaraj, *Curr. Res. Green Sustainable Chem.* **4**, 100140 (2021).

[96] Y. Yang and M. W. Urban, *Adv. Mater. Interfaces* **5**, 1800384 (2018).

[97] J. G. Kirkwood, *Chem. Phys.* **2**, 351 (1934).

[98] S. Nakano, Y. Yamahashi, F. Kaneko, T. Zushi, T. Mabuchi, T. Kawamura, and T. Tada, *KGK-Kautsch. Gummi Kunstst.* **74**, 56 (2021).

[99] M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, and J. S. Moore, *Chem. Rev.* **109**, 5755 (2009).

[100] Z. Huang and R. Boulatov, *Chem. Soc. Rev.* **40**, 2359 (2011).

[101] M. Encina, E. Lissi, M. Sarasua, L. Gargallo, and D. Radic, *J. Polym. Sci.: Polym. Lett. Ed.* **18**, 757 (1980).

[102] K. L. Berkowski, S. L. Potisek, C. R. Hickenboth, and J. S. Moore, *Macromolecules* **38**, 8975 (2005).

[103] G. Lake, A. Thomas, and C. Lawrence, *Polymer* **33**, 4069 (1992).

[104] W. Wong, T. Guo, and L. Cheng, *Int. J. Mod. Phys. B* **24**, 295 (2010).

[105] E. Elmukashfi and M. Kroon, *Int. J. Fract.* **177**, 163 (2012).

[106] H. Zhang, A. K. Scholz, J. de Crevoisier, D. Berghezan, T. Narayanan, E. J. Kramer, C. Creton, *J. Polym. Sci., Part B: Polym. Phys.* **53**, 422 (2015).

[107] G. Weng, A. Chang, K. Fu, J. Kang, Y. Ding, and Z. Chen, *RSC Adv.* **6**, 8406 (2016).

[108] S. Fakirov, *eXPRESS Polym. Lett.* **15**, 88 (2021).

[*Received June 2022, Revised September 2022*]