Chapter 2
Healing Agents Used for Mechanical Recovery in Nanotextured Systems

Several main healing agents currently used in self-healing nanotextured materials are discussed in this section. These include dicyclopentadiene (DCPD) and Grubbs' catalyst (Sect. 2.1) and dimethyl siloxane (DMS, a resin monomer) and dimethyl-methyl hydrogen-siloxane (curing agent) polymerized as poly(dimethyl siloxane) (PDMS, Sect. 2.2). Several other elastomers used for self-healing are discussed in Sect. 2.3. Self-healing agents can also comprise epoxy-hardener systems (Sect. 2.4), and gels (Sect. 2.5). Multiple other materials used in self-healing systems based on different physicochemical principles are omitted here, and the reader is directed to the more comprehensive list compiled in Wypych (2017) and the references therein.

2.1 Dicyclopentadiene (DCPD) and Grubbs' Catalyst

The dicyclopentadiene (DCPD, $C_{10}H_{12}$) monomer has been used in several studies on self-healing, beginning with the original system reported by White et al. (2001), Brown et al. (2004), Mauldin et al. (2007) and Yerro et al. (2016). In self-healing nanotextured materials based on electrospun and solution-blown nanofiber mats, DCPD was used by Sinha-Ray et al. (2012) and Wu et al. (2013). Ring-opening metathesis polymerization (ROMP) is activated as the DCPD monomer makes contact with the solid-state Grubbs' catalyst ($C_{43}H_{72}Cl_2P_2Ru$) dispersed within the epoxy matrix (see Fig. 2.1). The DCPD monomer is highly stable, low in viscosity, and is insensitive to the presence of oxygen and water/humidity under the polymerization conditions (cf. van der Zwaag 2007). In addition, poly(dicyclopentadiene) (PDCPD) is available as a highly crosslinkable polymer with desirable mechanical properties, namely, high toughness and strength (Perring et al. 2010; Lenhardt et al. 2013). It should be emphasized that the need to disperse the solid-state Grubbs' catalyst within the composite matrix introduces an extra technological step in the use of DCPD monomer as a healing agent. This step can be avoided when using other healing agents, such as those discussed below.

A. L. Yarin et al., *Self-Healing Nanotextured Vascular Engineering Materials*, Advanced Structured Materials 105, https://doi.org/10.1007/978-3-030-05267-6_2

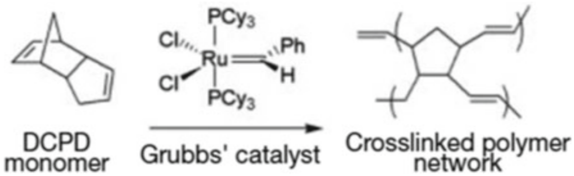

Fig. 2.1 Polymerization of DCPD activated by Grubbs' catalyst. Reprinted with permission from White et al. (2001)

2.2 Poly(Dimethyl Siloxane) (PDMS)

PDMS is the crosslinked product of DMS (the resin monomer) and dimethyl-methyl hydrogen-siloxane (the curing agent). The chemical structure and curing process of PDMS are briefly explained in Fig. 2.2. The resin consists of dimethylvinyl-terminated dimethyl siloxane (CAS: 68083-19-2), while the curing agent consists of dimethyl-methyl hydrogen-siloxane (CAS: 68037-59-2). The resulting silicone elastomer reveals superior mechanical strength and elasticity, outstanding chemical properties, and good biocompatibility; it is used widely in microfluidic devices, medical applications, cosmetics, and food items (as an antifoaming agent). The PDMS elastomer was first used for self-healing in Cho et al. (2006) and Keller et al. (2007), where the two components of PDMS, namely, the resin monomer and the crosslinker (curing agent), were encapsulated within urethane microcapsules. Then, PDMS has also been employed in self-healing nanotextured materials. For example, the encapsulation of PDMS within co-electrospun beaded fibers was reported in Park and Braun (2010) (see Sect. 4.2). Furthermore, PDMS has been also employed in self-healing composites reinforced with nano- and microfibers in Lee et al. (2014a, b, 2015a, b, 2017b, 2018) and An et al. (2015). In the latter series of works, the two components of PDMS were encased separately within the cores of the core-shell [polyacrylonitrile (PAN) shell] fibers by co-electrospinning or emulsion spinning (cf. Sects. 4.2 and 4.3, respectively). This dual self-healing system comprising DMS resin monomer and curing-agent encapsulated in nanofibers was also subsequently used as a healing agent in Neisiany et al. (2016).

2.3 Other Elastomers

Rubber elastomers are also excellent candidates for use in self-healing materials because they offer bonding sites for functional groups on their backbone chains (Rahman et al. 2013). Bromobutyl rubber (BIIR), synthetic material mostly used for automobile tires, also showed the reversible healing of cracks or cut pieces (Das et al. 2015; Lee et al. 2017a). The recovering mechanism is similar to the supramolecular one. Namely, the cut ends of rubber segments are rearranged by dynamic ionic association and thus physically crosslinked to each other. BIIR can be formed as a

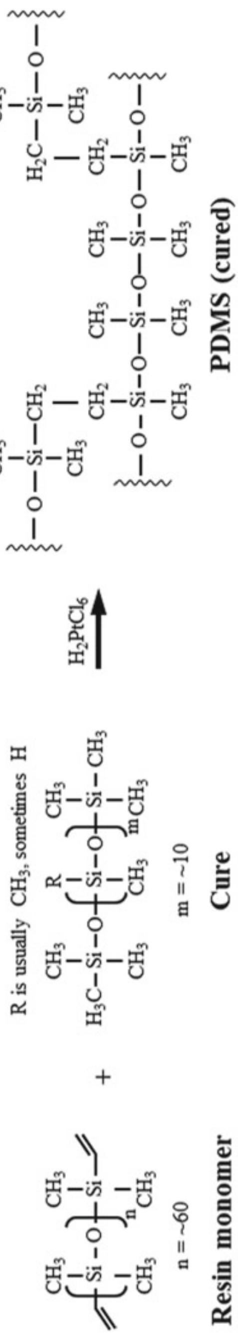

Fig. 2.2 Chemical structure and curing process of PDMS. Reprinted with permission from Campbell et al. (1999)

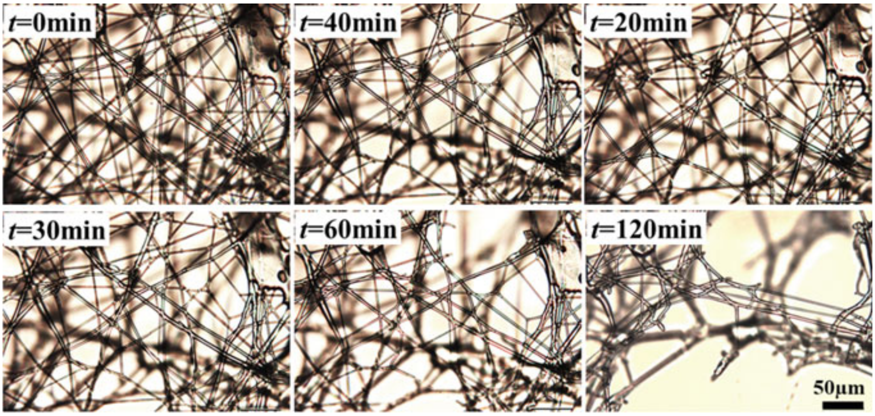

Fig. 2.3 BIIR fibers spun by solution blowing

thin film (Lee et al. 2017a) or a fiber (Fig. 2.3) by solution casting or solution blowing (Sect. 4.4), respectively.

Poly(butyl acrylate) films showed self-healing adhesion as the material coalesced and adhered to the contact interface (Faghihnejad et al. 2014). A low-melting-point polyimide ($T_m < 200$ °C) has been developed for the applications in wire insulation, coatings, and adhesives with self-healing properties (Jolley et al. 2012). Poly(methyl methacrylate) (PMMA) is another thermoplastic material that mechanically heals by the dynamic hydrogen bonding of the polyacrylate-amide (PAA) matrix without external stimuli (Chen and Guan 2015). Hydrogels composed of cellulose nanofibrils, poly(vinyl alcohol) (PVA) and borax have shown autonomous self-repairing abilities by the reformation of mobile hydrogen bonds (Spoljaric et al. 2014).

Polyurethane (PU) is one of the most popular mass-produced plastics. It can be formed as rigid panels or flexible foams for many applications including freezer insulation, mattresses, adhesives, and sports gear, etc. Traditionally PU is obtained by reacting isocyanate with polyol. Isocyanate is another extrinsic self-healing material that recovers broken bonds facilitated by water molecules (Sinha-Ray et al. 2012; Wang et al. 2014). Isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI) encapsulated in PU microcapsules have also been used in protective coatings (Yang et al. 2008; Huang and Yang 2011; Wang et al. 2014; Xiao et al. 2017). These compounds react with water vapor in the atmosphere, and thus show great potential as catalyst-free healing agents. The healing chemistry of diisocyanate monomers in contact with atmospheric moisture as the crosslinking agent is illustrated in Fig. 2.4.

The Diels–Alder reaction was used for heat-stimulated PUs in self-healing polymeric materials (Turkenburg et al. 2015). Acrylated polycaprolactone PUs were used in UV-cured self-healing coatings (Lutz et al. 2015). Zwitterionic multi-shape-memory PUs showed suitable shape-recovery properties (Chen et al. 2015b; cf. Fig. 2.5).

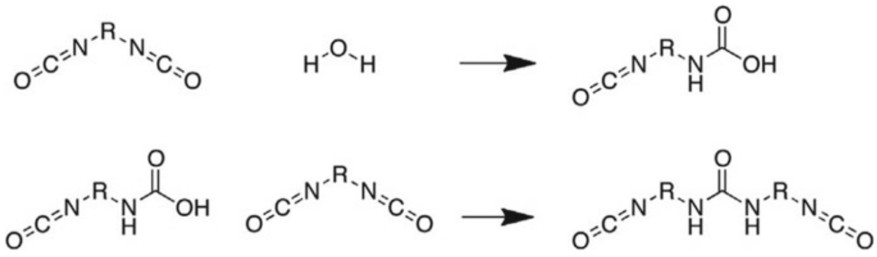

Fig. 2.4 Basic mechanism of moisture-assisted curing of diisocyanate monomers. Reprinted with permission from Keller et al. (2013)

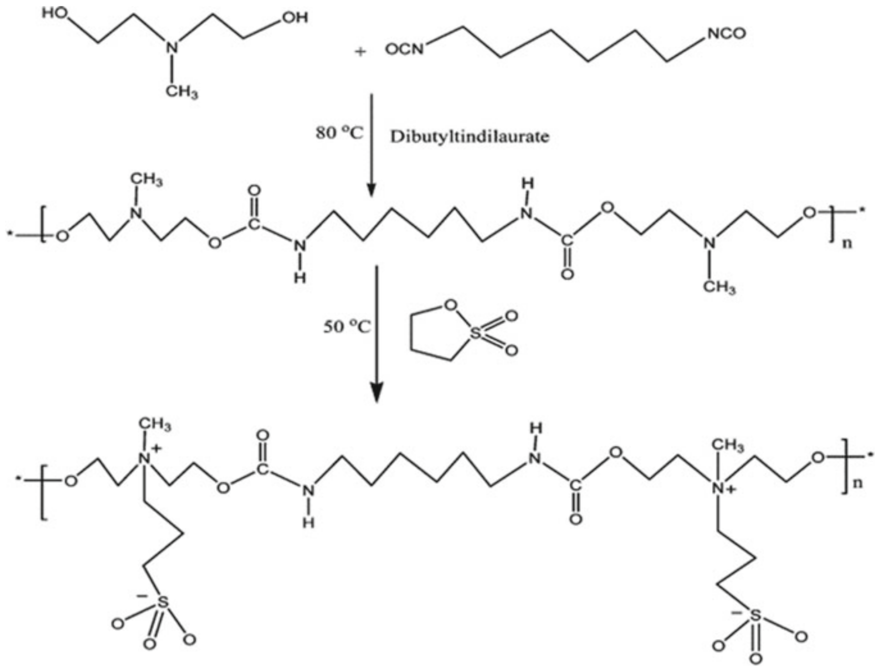

Fig. 2.5 Synthetic route toward zwitterionic shape-memory PUs (Chen et al. 2015b)

Thermoplastic PU containing carbon nanotubes showed autonomous healing requiring no intervention, i.e., an intrinsic healing process without the addition of any healing agents to the composite matrix, and a reversible healing that permits multiple healing events (Harmon and Bass 2014). Commercial polybutadiene can be modified to provide healing ability by the chemical Diels–Alder reaction (Bai et al. 2018; cf. Fig. 2.6), dual crosslinking with a transient network (Gold et al. 2016), and blending with a ring-opening agent (Jasra et al. 2015), among other mechanisms. Poly(ε-caprolactone) functionalized by the Diels–Alder reactions also shows thermo-reversible self-healing. The temperature increase induced by Joule heating

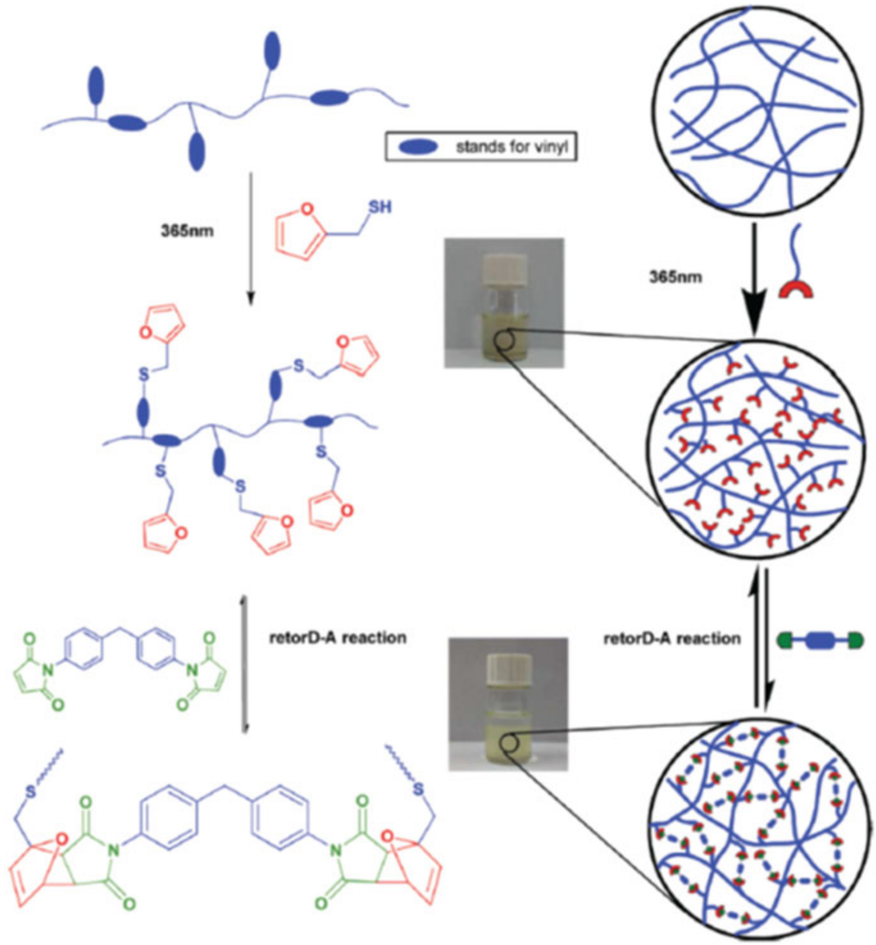

Fig. 2.6 UV reaction process used to prepare recyclable polybutadiene systems (Bai et al. 2018)

promotes chain mobility and heals cracks in the material within 3 min (Willocq et al. 2016).

Shape memory polymers (SMPs) can contract in response to localized heating. Accordingly, SMP fibers embedded in a matrix can span cracks that form in the matrix, essentially acting as springs (Li et al. 2013); see Sect. 1.5. Commercial fishing line and thermoplastic particles have been used to mimic muscles, with the line and particles spanning cracks as springs (Zhang and Li 2015); cf. Sect. 1.5.

2.4 Bisphenol-A-Based Epoxy and Other Types of Epoxy

From the perspective of materials properties, PDMS is among the most attractive self-healing agents owing to its aforementioned advantages. However, it normally requires a period of 24–48 h for full curing at room temperature. Furthermore, cured PDMS is soft and flexible. Accordingly, PDMS is not suitable for many applications, and other self-healing materials with a shorter curing times and higher strengths or greater stiffness are desirable. For this reason, the diglycidyl ether of bisphenol A (DGEBA, $C_{21}H_{24}O_4$), which comprises epichlorohydrin and bisphenol A (BPA, $C_{15}H_{16}O_2$) (Goosey 1985) and constitutes almost 90% of the global epoxy resin market (Raquez et al. 2010), has been used as a healing agent in several studies, mostly using microcapsules (Denq et al. 1999; Garcia et al. 2007; Blaiszik et al. 2009; Chen et al. 2013; Patrick et al. 2014; Jones et al. 2015; Vahedi et al. 2015). The likely reaction mechanism of DGEBA and diethylenetriamine (DETA) is illustrated in Fig. 2.7 (Farquharson et al. 2002). In addition, BPA epoxy resin diluted with neopentyl glycol diglycidyl ether (NGDGE) was used as a healing agent in Vahedi et al. (2015). However, BPA is also being gradually replaced with environmentally friendly materials because of its toxicity and related public health concerns (Flint 2012).

Ultimately, a BPA-based commercial epoxy was also employed as a healing agent embedded within solution-blown nanofibers and self-healing nanotextured materials based on them (Lee et al. 2016a, b, c; Neisiany et al. 2016). The epoxy used in the latter group of works set in 5 min and cures fully within 1 h. Note also that Zhang et al. (2014) and Zhang and Yang (2014) used DETA as an amine curing agent for cure the base epoxy.

Epoxy resins have experienced great development beginning in the early 20th century. Adhesives using epoxy are applied in almost every area of industry and daily life, because they offer reliable chemical and mechanical properties. Moreover, commercial epoxies are excellent candidate healing agents because they have wide ranges of physicochemical properties, such as adhesion strength, set and curing time, working temperature, and shelf-lifetime. The two-component epoxy system comprising a resin and curing agent (hardener) is in common use. Both components are stable and kept separately until they are mixed. Such dual components can be encapsulated in separate capsules, and are cured as the capsules rupture and their contents are mixed together. The healing chemistry and the release and curing process of such healing agents can be controlled by choosing different epoxies. For self-healing applications, the dual components of such epoxies can be stored in hollow tubes (Saeed et al. 2016), nano- or microfibers (Lee et al. 2016a, b) or microcapsules (Zhang et al. 2014) embedded in composite materials. In addition, the acrylic resin elastomer possesses autonomic self-healing ability based on hydrogen bonding entanglement and chain diffusion (Fan and Szpunar 2015). A palm oil-based alkyd was also used as a healing agent for epoxy resin (Shahabudin et al. 2016).

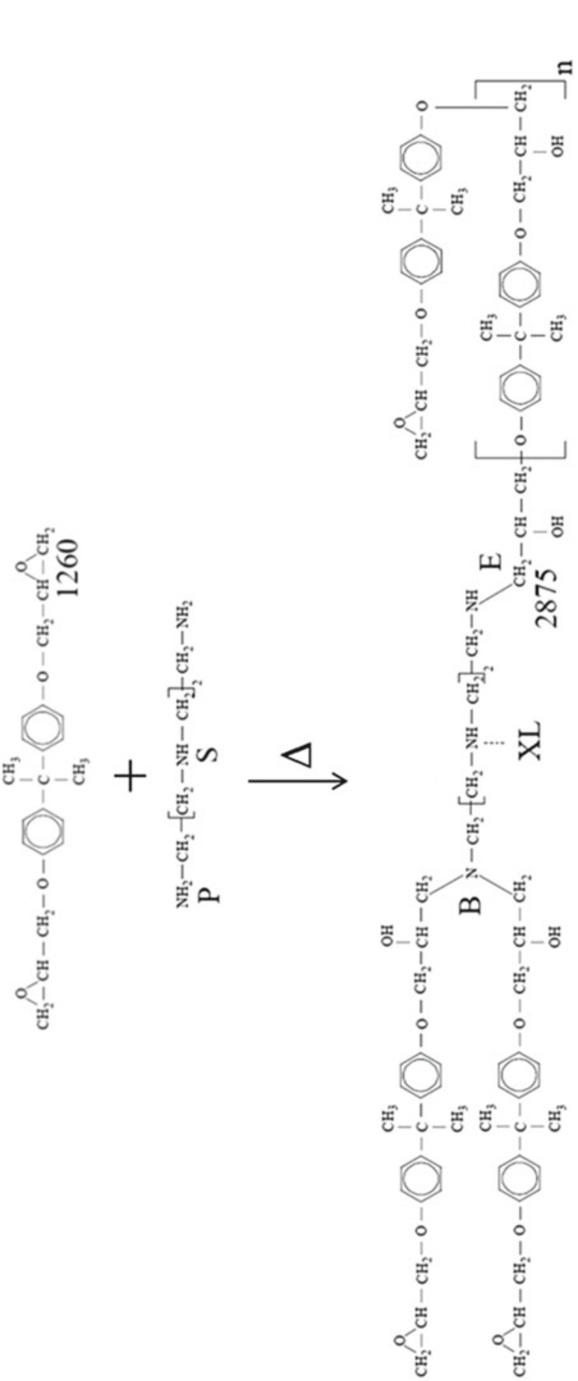

Fig. 2.7 Chemical structures of DGEBA and DETA and the corresponding curing reaction. P is the primary amine, E indicates chain extension, B indicates branching, and XL indicates crosslinking

2.5 Gels

Cellulose, which is suitable for grafting and blending with other materials, can be combined with chitosan to show gel-healing characteristics (Abdul Khalil et al. 2016). As a green material, chitosan is an especially promising candidate for self-healing under UV radiation or changes in pH (Urban and Ghosh 2015; Ou et al. 2015). Supramolecular polymeric hydrogels possess intrinsic self-healing characteristics based on the host–guest interactions, i.e., cyclodextrin and α-bromonaphthalene can act as the host and guest, respectively (Chen et al. 2015a).

White et al. (2014) demonstrated a regenerative-like approach that restored large-scale damage using shape-conforming dynamic gel components (gelator A/B, catalyst, initiator, promoter, and monomer), which are polymerized upon release into a crack.

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