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Thermoreversible Polymeric Nanocomposites

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Abstract

Polymeric nanocomposites are widely used in applications such as structural materials, electronics, energy, and biomedical as they synergistically combine the desired properties of the filler and the polymer. The emergent properties can be designed and tuned based not only on the choice of filler and polymer but also on the type of bond and interface created between the two components. When the bond between the two is covalent, the nanocomposites have superior mechanical characteristics. When this covalent bond is reversible, a combination of high impact resistance and high tensile strength is achieved. A well-known approach to achieve these reversible covalent bonds is via the Diels-Alder reaction between a diene and a dienophile. At elevated temperatures, the retro Diels-Alder reaction is dominant resulting in bond cleavage. This chapter reviews the different strategies involving Diels-Alder reactions at the polymer-filler interface. Various fillers have been researched including silica, carbon nanotubes, and graphene, which impart different mechanical and conductive properties to the nanocomposite. A variety of polymer matrices have been reported by various researchers and are summarized here. The choice of diene and dienophile influences the rate of reversible reaction and thus the final properties as will be discussed.

Keywords: nanocomposites, thermally reversible interactions, Diels-Alder, graphene, carbon nanotubes

1. Introduction

Polymeric composites are all around us. The addition of nanofillers to polymers has opened pathways for designing materials with improved functionalities. The synergistic effects of each component can result in better mechanical properties, thermal or electrical conductivity, and enhanced optical properties. The wide range of applications, spanning diverse fields such as civil engineering (building and constructions), electronics, biomedical materials, etc.,

renders this kind of materials essential for our daily life. The simplest structure of a composite is the one consisting of a polymeric matrix in which a solid filler is dispersed. The logic behind this combination is the ability to manipulate the composite properties as function of those of the individual components and the interfacial bonding [1]. However, even at this very simple level, the system can be considered as quite complex. In particular, the geometrical shape of the filler as fibers, platelets, and particles (respectively approached as 1-, 2-, and 3-dimensional objects) is pivotal in determining the final properties. Many studies have been dedicated in the past to understand these features and to develop physical models that are able to predict the properties as a function of the structure [2–8].

One of the challenges in nanocomposites is the nanoscale dispersion and distribution of the filler, which can be achieved by chemical modification of the filler surface. During the last three decades, many works have been focusing on a relatively novel concept, i.e., on the use of a covalent, yet thermally reversible, linkage between the filler and the matrix. On the one hand, this fits the general idea that (thermally) reversible linkages between the components could significantly improve some mechanical characteristics, such as impact properties. This can be achieved also by using relatively weaker interaction forces, such as hydrogen bonding. On the other hand, the use of covalent, and yet reversible bonds, might significantly help in achieving the same goal while avoiding any significant compromise on the strength of the final material [9, 10]. Indeed, among all possible thermoreversible interactions, only covalent bonds can be defined as relatively strong (more than a few kcal/mol) and metal free (**Figure 1**).

Hydrogen bonding [11–14] and ionic interactions [9] have been often used as thermally reversible interactions for composites of different kinds. One of the main driving forces behind the use of such a strategy is the presence of special end properties. For example, the dynamic nature of thermally reversible interactions (as a function of temperature) endows composites with self-healing behavior [11, 13, 15–17] and shape-memory characteristics [18, 19].

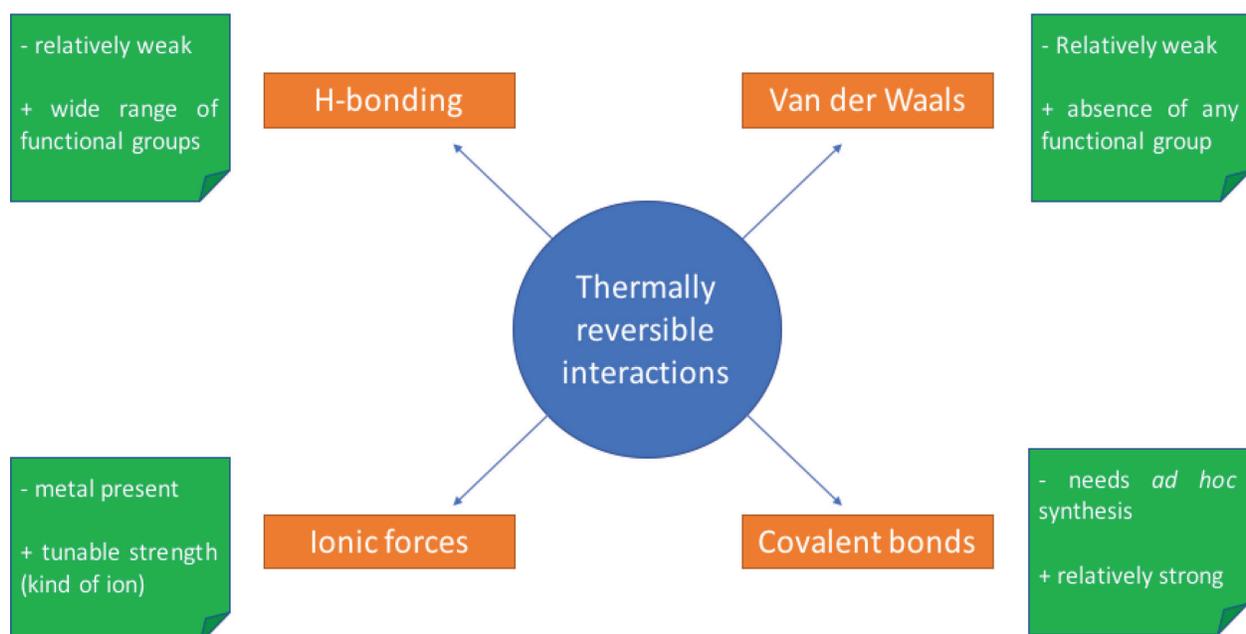


Figure 1. Schematic representation of different kinds of thermally reversible interactions.

Furthermore, the same kind of reversible chemistry can be also applied in solution [20–22] where the crosslinking yields gels of different nature finding applications in very popular fields such as biomedical products. It must also be stressed that very recently particular attention has been paid to a new research field, still in its infancy, dealing with the use of supramolecular polymer in composites [23, 24]. The overall concept, stemming from the use of reversible interaction for the polymer backbone, nicely fits in the thermally reversible context although with even more remarkable loss of properties at relatively high temperatures. In the present chapter, we focus on the use of the Diels-Alder (DA) reaction as a modification toolbox for nanocomposites. While presenting a general overview of the recent literature, we aim to highlight the strategic chemical modification routes and, whenever possible, the added value of such strategy for the properties of the final composite. Other kinds of “click” reactions are also possible, the reader being referred to recent works in the field [25].

2. Chemical strategies for the insertion of DA groups in nanocomposites

The use of Diels-Alder chemistry as a modification tool for composite materials stems from the peculiar characteristics of this reaction. The choice to proceed with or without catalyst at relatively mild temperatures as well as the intimate connection between the forward (DA) and reverse, i.e., retro Diels-Alder (rDA) reactions and the structure of the diene and dienophile render this reaction ideal in terms of being able to control its decrosslinking as a function of temperature. As a consequence, many efforts have been reported in the use of DA to decorate various types of fillers including carbon nanotubes (CNT) [20, 26] and silica [27, 28]. In particular, CNT represent a popular choice (**Figure 2**) in view of their increasing availability and the kaleidoscopic variety of properties they potentially endow the composite with (electrical conductivity, strength, and shape memory).

Functionalization of CNT improves their dispersion in polymer matrices and also improves the processability of the nanocomposites. The DA reaction has a clear effect on the debundling of CNT [29] and also on their dispersion in polymeric matrixes [33]. The mechanical property enhancement is due to two mechanisms: the fillers act as (additional) crosslink points while also serving as stress-transfer points, distributing the stress to the polymer matrix uniformly. In both cases, the key feature is the improved adhesion at the interface between filler and matrix [34]. It is also noteworthy how CNT can act as both diene and dienophile in the DA reaction, respectively, with maleimide and furan groups [30]. As these reactions are mainly aimed at introducing functional groups on the CNT surface, this testifies the versatility of the approach even if in some cases side reactions might be present [19] and there is no mention of the reversibility or its use [31]. Some of the reported approaches towards incorporation of CNT via DA clearly indicate relatively easy synthetic routes [35] (**Figure 3**).

In the present case, functionalized CNT and furfuryl amine are simply mixed with di-glycidyl-bisphenol A, yielding in one step, a multifunctional monomer that can be subsequently cross-linked via addition of a bis-maleimide. In this case, the self-healing behavior can be induced by near-infrared (NIR) irradiation (**Figure 4**). Scratch healing was demonstrated in the vicinity of the

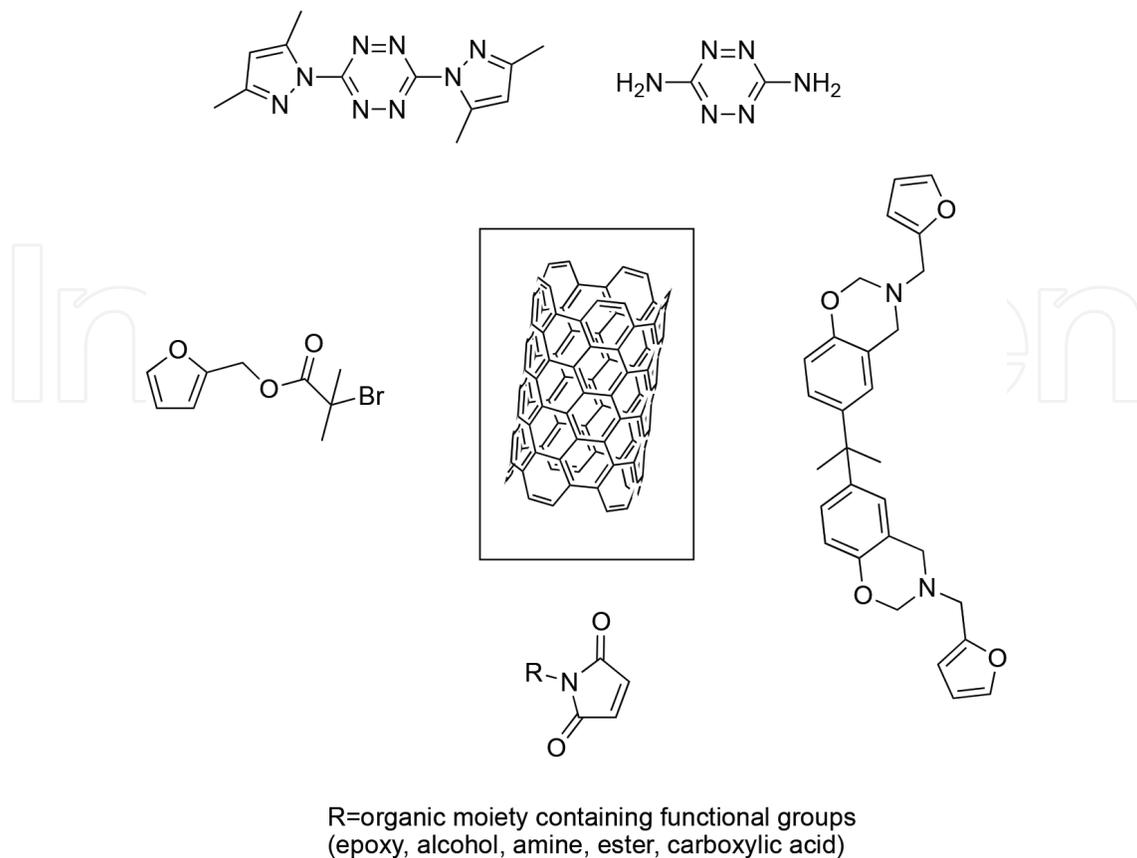


Figure 2. Schematic overview of CNT decoration via the DA reaction. Adapted and redrawn based on [29–32].

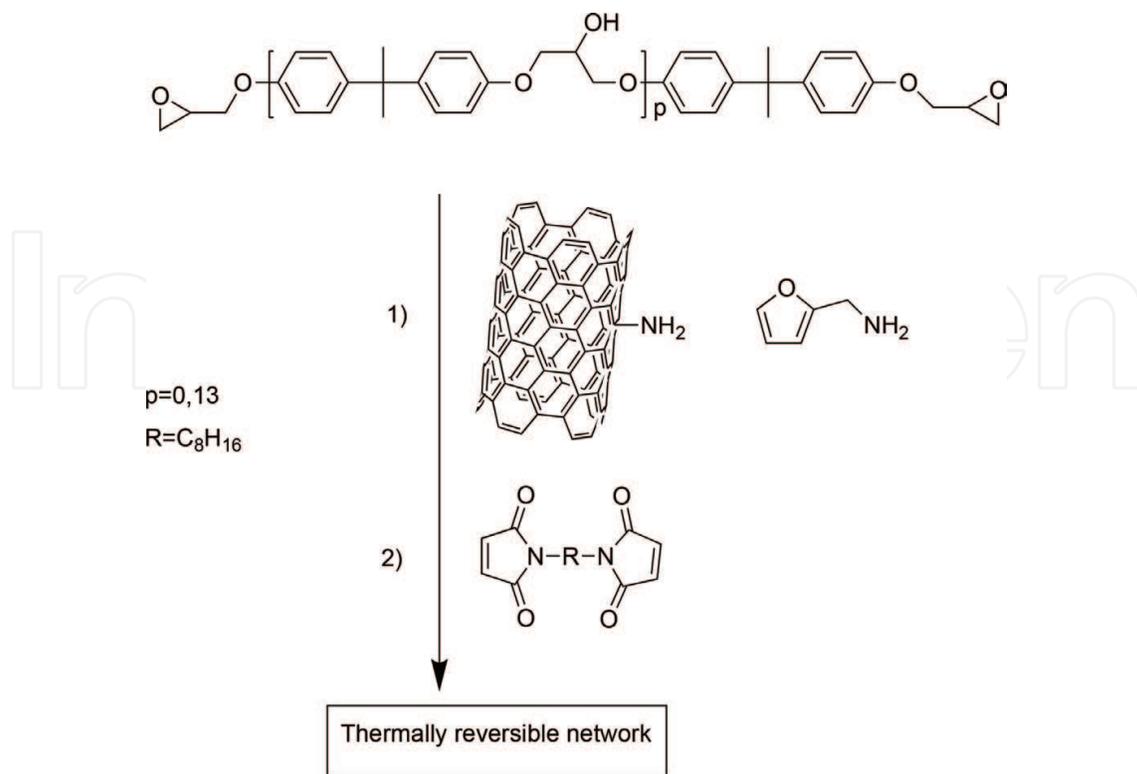


Figure 3. Simple incorporation of CNT into epoxy-like resin [35].

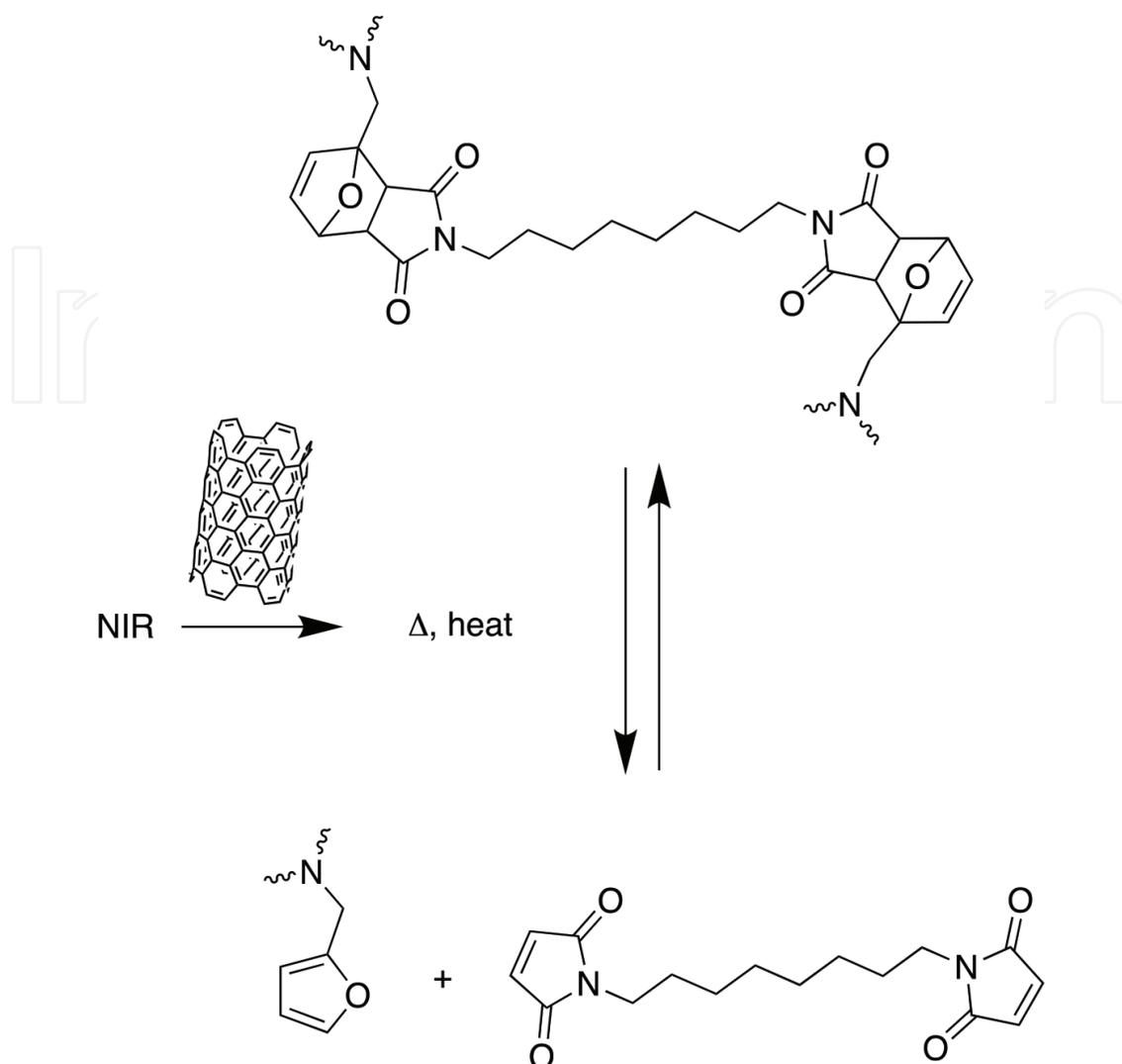


Figure 4. NIR induced self-healing process of epoxy resins [35].

damage using optical microscopy by optimizing the location and power of the laser source. The presence of the CNT ensured the overall robustness and integrity of the nanocomposite samples while also increasing the photothermal conversion efficiency, which enhanced self-healing.

CNT-polymer nanocomposites were demonstrated as reversibly bendable actuators in solvent detection sensors [34]. The incorporation of CNT was crucial in this work as they contributed toward the thermal and electrical conductivity necessary for this particular application. The reversible DA linkages comprising of furan and maleimide moieties ensured good adhesion between the dissimilar layers in the bilayer sensors. This concept of anisotropic expansion in different environments could be extended to multiresponsive materials with applications in soft robotics or self-deployable actuators in different stimuli such as moisture, solvents, pH, and/or temperature. Moreover, the incorporation at the same time of CNT with magnetic nanoparticles (**Figure 5**) is also possible via the DA approach [36].

In this case, the functionalization of Fe_3O_4 nanoparticles with maleimide groups is followed (route A) by DA reaction with CNT and finally by mixing with the polymeric matrix. In another approach [37] (route B), the functionalized nanoparticles can be directly embedded

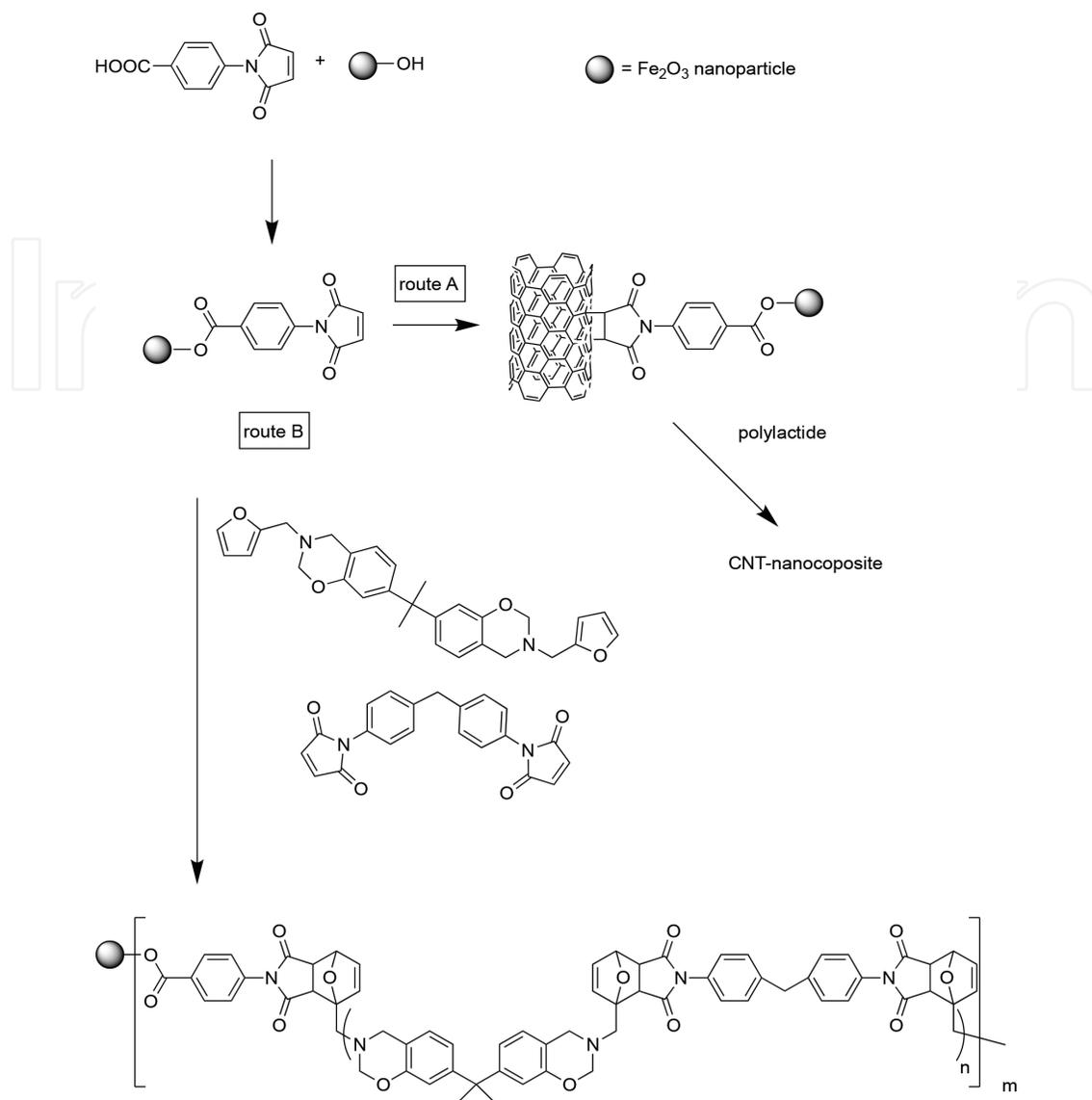


Figure 5. Preparation of composites based on CNT and magnetic particles [36, 37].

in a telechelic polymer via the DA reaction, thus yielding composites without CNT but with magnetic particles. The simplicity of these approaches is in stark contrast with the complex behavior, particularly the response to heat, electricity, and magnetic field. It is worth also noticing, for electrospun fibers produced in this way, the relevant toughening behavior, which might indeed be related to the thermally reversible interaction at the interface.

The extreme precision of the DA reaction, almost devoid of any side reaction, renders it particularly suitable also for simple decoration of different fillers. A recent example [38] is constituted by the synthesis of nanocomposites, forming gold particles and poly-*p*-phenylene ethynylene (**Figure 6**).

As expected, the good adhesion at the interface has a clear influence on the self-assembly behavior of the Au-nanoparticles, and peculiarly in this case, this improves the electronic communication between the conducting backbone and the nanoparticles. Other kinds of nanoparticles, with tailor-made structure and properties, have also been reported, particularly aiming

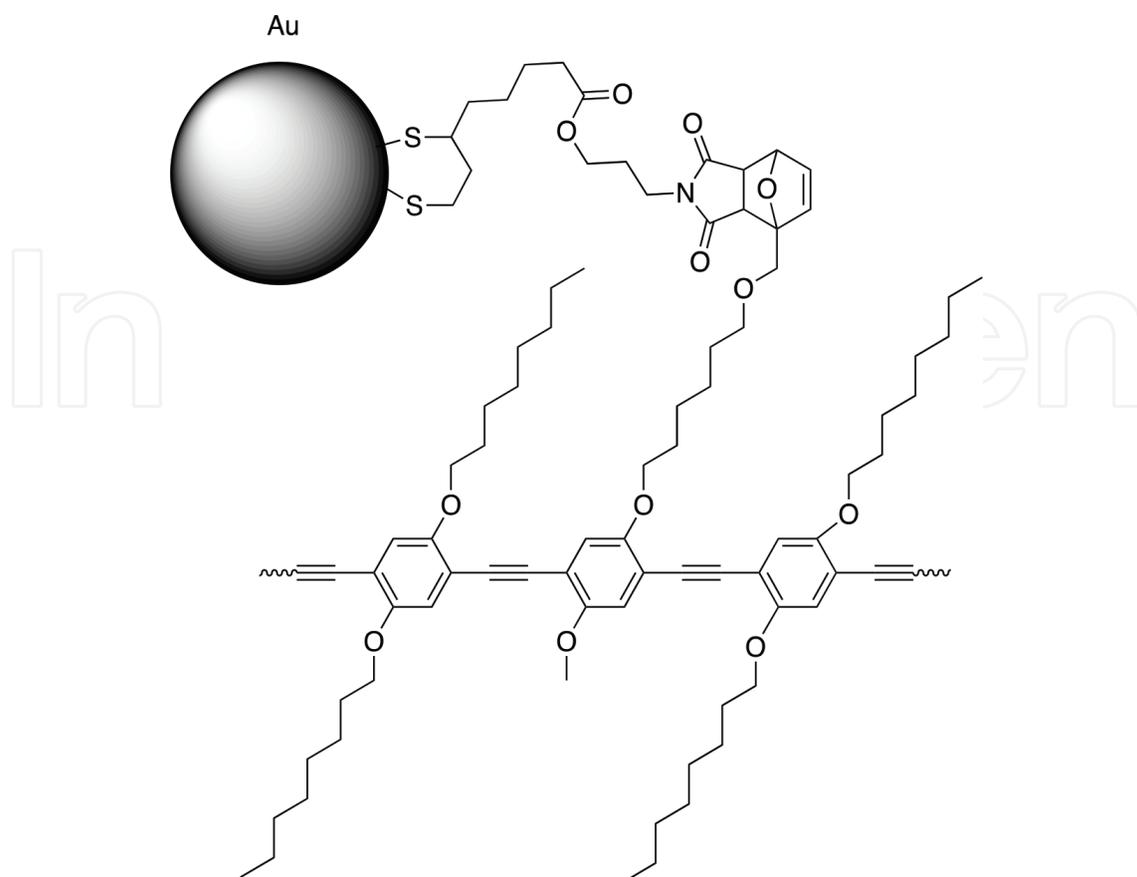


Figure 6. Maleimide functionalized gold (MA-Au)-nanoparticles-based composite [38].

at producing high- k nanocomposites for applications as motion sensors [39]. In this case, the dielectrical permittivity of the material is tunable as a function of the filler intake and can be systematically recovered upon self-healing of the corresponding films. The hybrid polymer-ceramic materials had an improved dielectric property and improved retention of capacitance due to the recoverable DA bonds. The specific capacitance was shown to restore up to 82% even after 10 cycles of cutting and healing. Thus, in addition to improved interfacial properties, the DA reaction also enables the lifetime extension of such materials during application. Functionalized nanoparticles (with DA groups) might have an important role as additives as they have been also employed as dynamic crosslinker in gels [40].

The same approach has been used for POSS-based composites [41] and polyesters (**Figure 7**). The partially crosslinked network was insoluble to common organic solvents while showing thermoreversibility at 120°C. The occurrence of the DA reaction between furan and maleimide functional groups was induced by melt mixing as opposed to casting. The resultant nanocomposites had significantly higher flexural and tensile moduli as well as glass transition temperature as compared to the polymer matrix. This mechanical behavior clearly highlights the dynamic nature of the bonds, while at the same time suggesting a synergy in terms of strength and impact properties.

Besides CNT and nanoparticles, graphene has also attracted much attention. This is not surprising when making allowances for the similar structure and reactivity of these two fillers. In one report, self-healing was achieved by catalyst containing microcapsules and graphene

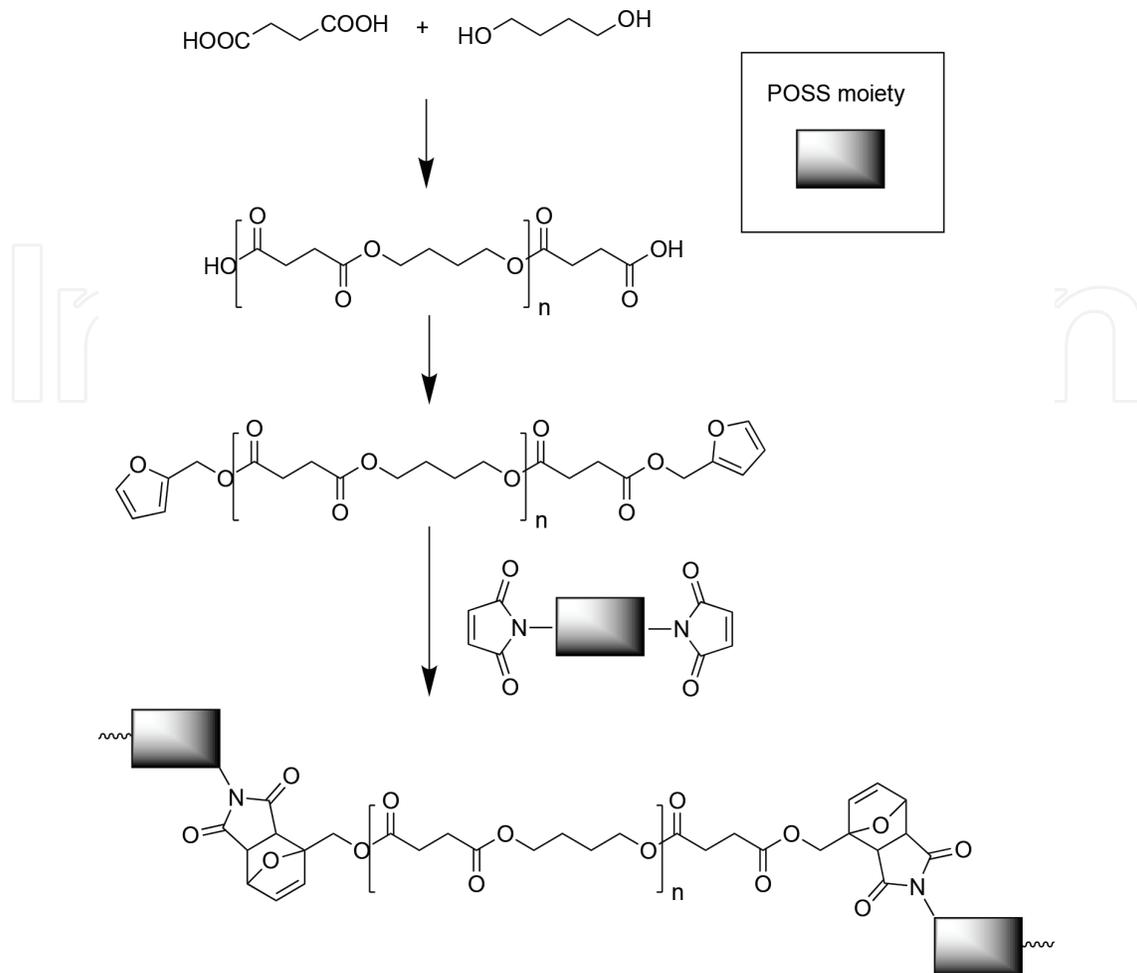


Figure 7. POSS-based composites [41].

was added to offset the reduction in tensile strength due to the addition of the weaker microcapsules [42]. Graphene-based nanocomposites have been reported for possible application as supercapacitors [43]. In this case, a conductive polymer polypyrrole was chosen due to its stability upon exposure to oxygen, cheap cost, and easy synthesis. Tetrazine derivatives were reacted onto reduced graphene sheets via the inverse electron demand Diels-Alder reaction. The nanocomposites showed good electrochemical properties and a small resistance due to easy ion accessibility and thus are promising as potential electrode materials for supercapacitors. Graphene-based nanocomposites have also been demonstrated as strain sensors for flexible electronics [44]. Here, furfuryl containing polyurethane was crosslinked with a bis-maleimide onto reduced functionalized graphene oxide sheets. The nanocomposites showed good flexibility, and thermal and electrical conductivity was required for the aforementioned application. Healing via rDA reaction was achieved by microwave heating in <5 min. A particularly simple approach (Figure 8) allows easy fabrication of composites based on graphene and a multifunctional DA crosslinker [45].

The mechanical behavior of the final product clearly reflects the pivotal role of the graphene intake (Figure 9). As expected, tensile strength and Young's modulus increase with the graphene intake while the elongation at break decreases.

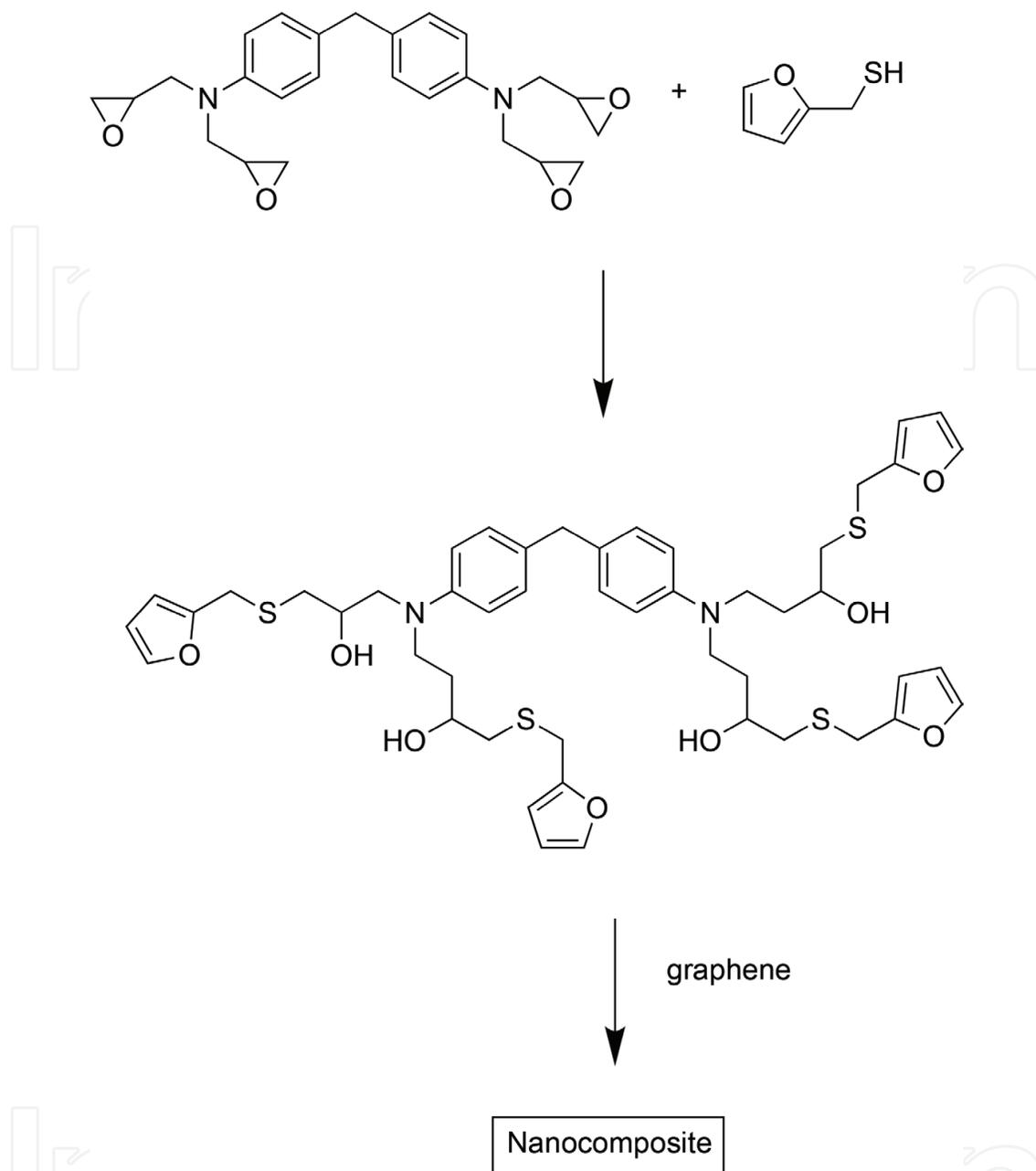


Figure 8. Nanocomposite fabrication via DA reaction between graphene and a multifunctional crosslinker.

Although in a different work [46], a significant improvement of the impact properties has also been reported and preliminarily attributed to the wave propagation through the graphene platelets. Also in the case of graphene, as for CNT, reactivity as diene or dienophile, can be exploited [47]. The occurrence of the reaction between graphene and the maleimide crosslinker is once more testified by the excellent dispersion of the graphene sheets within the matrix. These sheets act as a local thermal collector by converting adsorbed infrared or microwave energy into heat, thus triggering the reversible bond behavior. This renders the final composite responsive to multiple stimuli (heat, electricity, infrared, microwave) for self-healing and shape memory. These effects are then on top of the change in mechanical properties as, for example, highlighted above. Such improvement of mechanical behavior can also

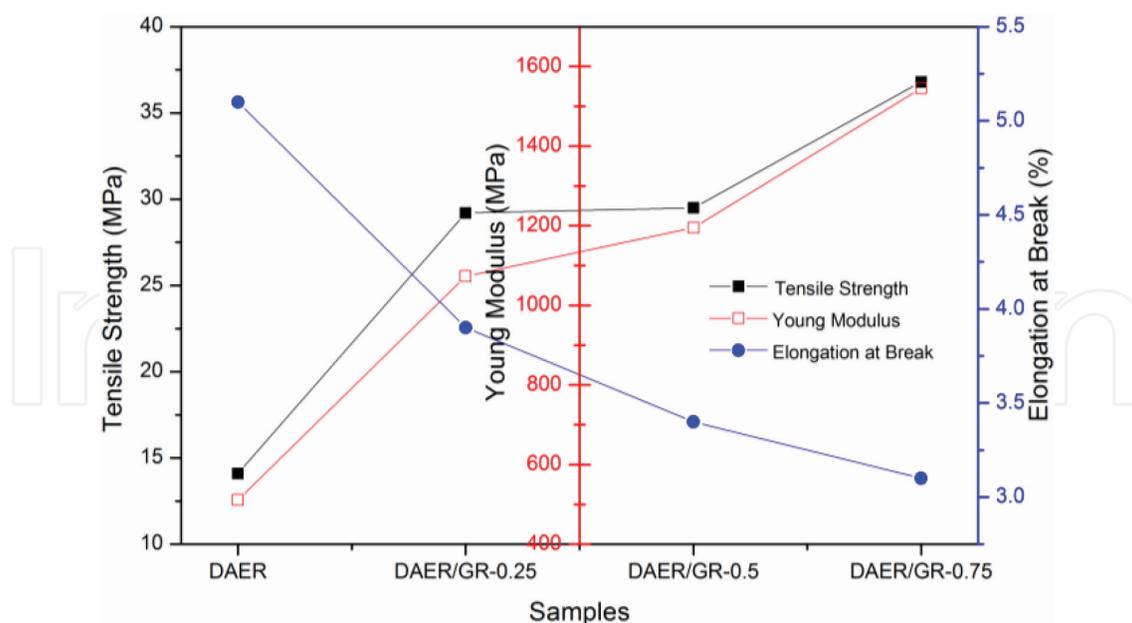


Figure 9. Mechanical properties of nanocomposites as function of the graphene intake [45].

be “dramatic” as reported in the case of styrene-butadiene rubber (SBR) functionalized with furan groups, mixed with furan-functionalized CNT and crosslinked by addition of a bis-maleimide [48]. In this case, a relevant increase (over 200%) in modulus values and toughness could be booked. This highlights once more the synergy in the combination of nanofillers and their thermally reversible adhesion to the matrix. The concept of “local” self-healing, for which nanoparticles play a crucial role, is actually broader than merely graphene and DA. The fact that heat can be generated locally renders the crosslinking kinetics faster [49] also in the case of ionic interactions and magnetic nanoparticles.

In addition to relatively novel nanofillers, composites with thermally reversible interactions have also been prepared based on more “classical” ones, such as silica [50] again with the general aim of inducing self-healing behavior. The general preparation strategy is similar to the ones presented above and entails the functionalization of the polymer and the filler with furan groups, followed by crosslinking with bis-maleimides [50]. However, in the special case of silica, also different approaches are possible in view of the possibility to obtain silica as result of sol-gel reactions (**Figure 10**).

Furan and maleimide groups are the most commonly used diene and dienophile in self-healing reversible systems. This is due to their high reactivity and low activation energy of the rDA reaction, which enables the rDA reaction to proceed around 100 to 140°C. In the majority of the examples illustrated so far, attention has been paid to the occurrence of the DA reaction while aiming at relatively low rDA temperature (typically 120°C) in view of self-healing properties at relatively mild experimental conditions. In some cases, a catalyst has also been used to achieve self-healing at even lower temperatures [51]. On the other hand, for some specific applications in extreme environments (e.g., in automotive or aerospace), thermal stability up to 200°C is a *conditio sine qua non*. This can be achieved by changing the chemical structure of the DA groups. A recent example involves the use of anthracene and maleimide groups [52] (**Figure 11**).

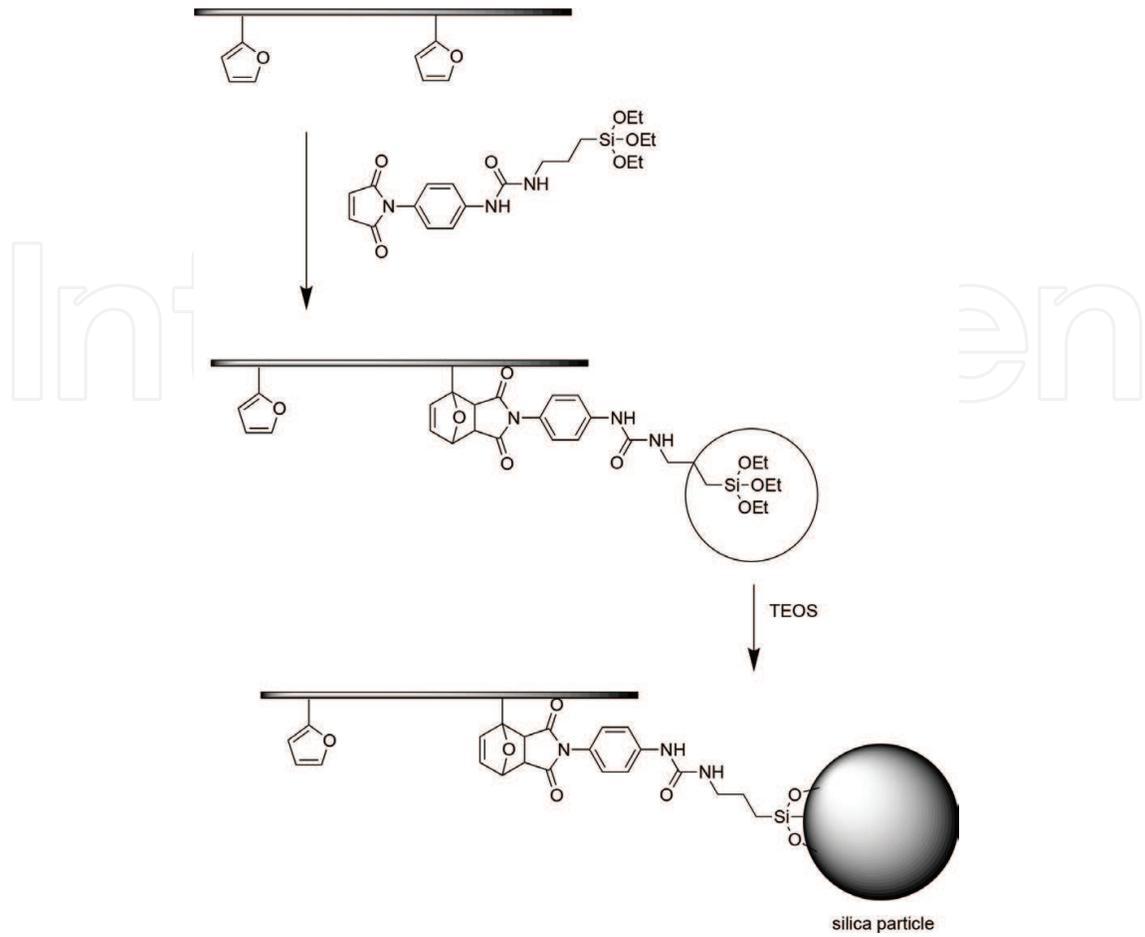


Figure 10. Sol-gel approach toward the synthesis of silica-based thermally reversible composites [50].

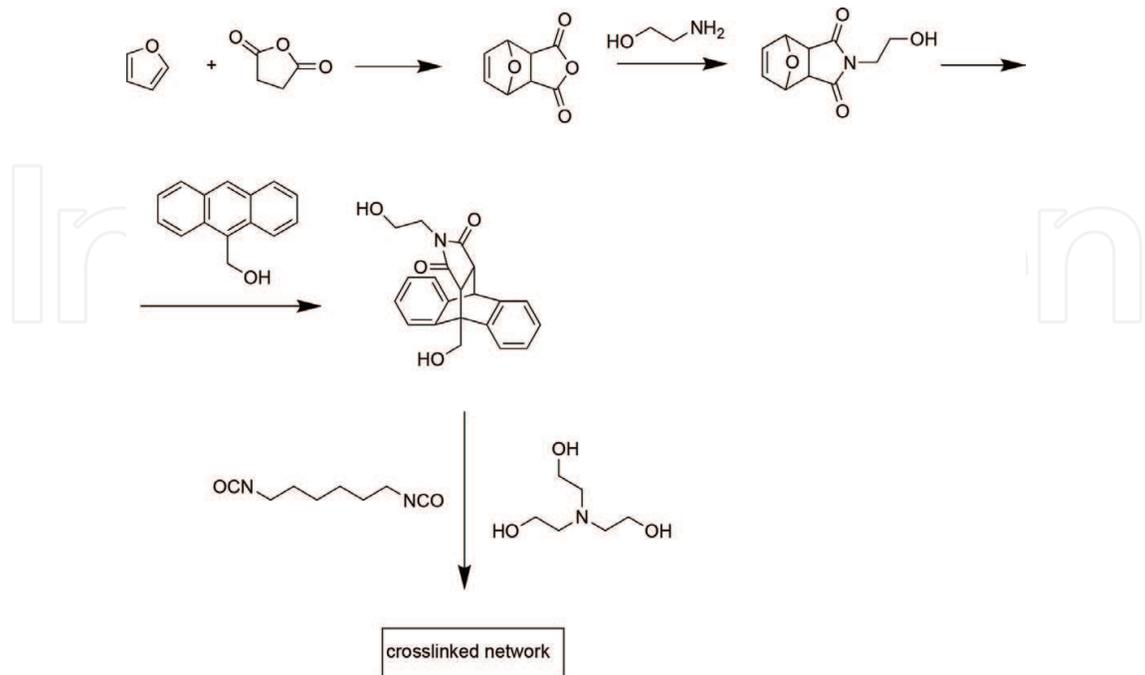


Figure 11. Anthracene-based composites [52].

The resulting polyurethanes (PU) show self-healing behavior by pure DA reaction for mechanically cleaved adducts. The use of continuous fibers also helped with mechanical robustness comparable to those of engineering polymers and structural composites. These materials were exceptionally thermally stable and showed high strength, stiffness, and toughness.

3. Future outlook

Thermal reversibility allows adding another tool for the design of smart composites. Properties such as self-healing and shape memory, besides the “classical effects” on thermal and mechanical ones, are easily added to the composite behavior. The sensitivity to multiple external stimuli such as electricity, irradiation, and heat [11, 18, 53, 54], represents a focal point for the design of smart materials. An added value in this case is the possibility (via irradiation) of remote-induced self-healing as well as of ultrafast kinetics [55]. In this context, it is conceivable that many research efforts will be spent in achieving a systematic control over this multifunctionality and responsiveness. In turn, this will require even more precise control over the kind of functional groups present and the chemical structure in more general terms. Further studies are then envisioned in the general field of structure-property relationships, for example, by a systematic investigation on the influence of spacers [56] on the DA decrosslinking. Other factors influencing the structure of the composite and thus its properties, such as the nature of the filler and the backbone, continue to represent points of attention. The possibility to extend the concept to inorganic polymers [57], the use of fullerene derivatives [58] as well the general trend toward the use of green fillers [59] have been recently reported, but deserve further study in order to explore all possible application fields. Finally, the combination of the properties highlighted above and their synergy with additional ones, such as color change upon thermally reversible behavior [60], constitute attractive characteristics of these materials.

Conflict of interest

The authors declare no conflict of interests,

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