Polymeric materials reinforced by noncovalent aggregates of polymer chains

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Abstract
Mechanical performances are among the most fundamental properties that dictate the applicability and durability of polymeric materials. Reinforcement of polymeric materials is eternally pursued to broaden the applications of polymers with light-weight, low-cost and easy-processing advantages. Noncovalent aggregates of biomacromolecules have been found to play a significant role in the mechanical properties of many natural materials, such as the spider silk. Increasing numbers of reports have demonstrated that the in situ formed noncovalent aggregates of polymer chains in polymeric systems are highly effective for enhancing the mechanical properties of artificial polymeric materials, in terms of strength, stiffness, toughness, and/or elasticity. The in situ formed noncovalent aggregates act as additional crosslinking domains and well-dispersed “hard” nanofillers in the polymer networks, significantly strengthening, stiffening and/or toughening the polymeric materials. Moreover, the noncovalent crosslinking of polymer chains favors the development of healable and recyclable polymeric materials, thanks to the reversible and dynamic properties of noncovalent bonds. This review provides an overview of the recent advances on the enhancement of the mechanical properties of different polymeric materials by the in situ formed noncovalent aggregates of polymer chains. It is expected to arouse inspirations for the development of novel polymeric materials with extraordinary mechanical performances and functionalities.

KEYWORDS
aggregates, noncovalent bonds, polymeric materials, self-healing materials, supramolecular materials

INTRODUCTION
Since the concept of macromolecules was reported in 1920,[1] research in polymers has made triumphant progress and polymeric materials have become indispensable in our daily life and engineering applications. Due to the light-weight, low-cost and easy-processing advantages, polymeric materials have been the substitutes for traditional metallic and ceramic materials in enormous applications. Mechanical performances are among the most fundamental properties that dictate the applicability and durability of polymeric materials. New polymeric materials with ever-higher mechanical performances are eternally pursued. Reinforcement of polymeric materials is a constant project for researchers and engineers in the field of polymers. Two types of strategies have mainly been well established and widely employed to reinforce polymeric materials.[2–4] The first lies in intrinsic regulation of the configuration of polymer chains and the structure of polymer networks to restrain the mobility of polymer chains upon load, such as alignment and crystallization of polymer chains, interpenetration of polymer networks, double-network crosslinking, and so forth.[5–13] The second relies on the extrinsic incorporation of rigid nanofillers into the polymer matrices, wherein the nanofillers include inorganic and organic nanomaterials, such as silica,[14–16] clays,[17–20] glass fibers,[21] carbon nanomaterials,[22–26] cellulose nanocrystals,[27,28] and so forth.[29–31] The as-described intrinsic and extrinsic strategies can be combined to synergistically enhance the mechanical performances of the resultant polymer composites. Homogeneous nanofiller dispersion and good compatibility between the nanofillers and the polymer matrices are crucially important for the effective reinforcement of polymer–nanofiller composites.[32,33] Unfavorably, the externally incorporated nanofillers generally tend to aggregate in the polymer matrices owing to their large specific surface area and high surface...
FIGURE 1  Schematic illustration of the spontaneous noncovalent aggregation of polymer chains in polymeric systems involving different noncovalent interactions, such as electrostatic, H-bonding, coordination and hydrophobic interactions. The in situ formed noncovalent aggregates act as additional crosslinking domains and “hard” nanofillers that can effectively enhance the mechanical properties of the resultant polymeric materials.

Nature has developed many miraculous materials with extraordinary mechanical performances reinforced by the in situ formed noncovalent aggregates of biomacromolecules. Spider silk and byssus cuticle of mussels are two typical natural materials that exhibit extraordinary combination of high strength and high toughness, whereas comparable mechanical performances are highly challenging to achieve for artificial materials. It has been found that the exceptional mechanical performances of spider silk and byssus cuticle of mussels predominantly benefit from their unique two-phase structures, which are formed because of the noncovalent aggregation of protein chains. Specifically, the hydrogen-bonded (H-bonded) β-sheet nanocrystals in spider silk and the granules consisting of dopamine-Fe³⁺ crosslinks in byssus cuticle of mussels are the dominant contributors to their extraordinary mechanical performances. Inspired by the reinforcement effect of noncovalent aggregates in natural materials, our group has recently developed a series of high-performance noncovalently crosslinked polymeric materials involving in situ formed noncovalent aggregates of polymer chains. We have systematically investigated the correlation between the characteristics of the noncovalent aggregates and the mechanical properties of the as-developed polymeric materials. Accordingly, the composition, structure, and dispersion of the aggregates can be reasonably designed and tailored to significantly enhance the mechanical properties of the polymeric materials, in terms of strength, stiffness, toughness and/or elasticity (Figure 1). Compared to the externally incorporated nanofillers, the in situ formed polymer aggregates exhibit superior compatibility and strong interactions with the polymer matrices. Therefore, the aggregates can work as additional crosslinking domains and in situ formed “hard” nanofillers of the polymer matrices, reinforcing the polymeric materials more effectively (Figure 1). Furthermore, thanks to the reversibility of the noncovalent crosslinking, the as-developed high-performance polymeric materials are intrinsically healable and/or recyclable. The healability and recyclability can significantly enhance the reliability and extend the service life of the polymeric materials, endowing them with high sustainability. This review article summarizes the recent achievements from our and other groups on the reinforcement of polymeric materials via noncovalent aggregates of polymer chains. We will highlight examples of different categories of polymeric materials reinforced via this mechanism, including plastics, elastomers, and hydrogels, developed by different methodologies. This Review article not only provides new perspectives in the development of...
polymeric materials with high mechanical performances, but also gives deep insights in the composition-structure-property relationship of polymers.

DIFFERENT CATEGORIES OF POLYMERIC MATERIALS REINFORCED BY NONCOVALENT AGGREGATES

According to the mechanical features and composition, polymeric materials can be classified into different categories. Plastics and elastomers are dry polymeric materials, while hydrogels contain a large amount of water. Plastics generally have higher stiffness (i.e., Young’s modulus), lower extensibility, and smaller elastic deformation region compared to elastomers, while hydrogels are generally soft and highly deformable materials. Therefore, the structures of the polymer networks for plastics, elastomers, and hydrogels are different to some extent, while similar principles are shared for the enhancement of their mechanical performances. We will highlight the enhancement effect of the noncovalent aggregates on different aspects of mechanical properties for plastics, elastomers, and hydrogels, respectively, in this Review article.

Plastics

Plastics have tremendous applications spanning from our daily necessities to military and aerospace due to their high strength-weight ratio and easy processability. A plastic can maintain its shape under a certain load like metal and ceramic materials. Therefore, plastics allow small elastic/restorable deformation (<10%), beyond which the material undergoes fracture or inelastic/unrestorable deformation. Plastics must operate below their glass transition temperatures if amorphous, below the melting temperature if crystalline, or have a crosslinking density that is sufficient to maintain its shape. Compared to the traditional metallic and ceramic materials, plastics generally exhibit lower mechanical performances, in terms of strength, stiffness, and/or toughness. Therefore, on one side, development of high-performance plastics is always a crucial goal in polymer research to broaden the applications of polymers. On the other side, the pervasive environmental threat posed by plastics urges the development of healable and recyclable plastics with high sustainability. Recently, our group has developed the development of healable and recyclable plastics with extraordinary mechanical performances. The recent progress in this aspect will be described in this part.

Polymer complexes can be formed by mixing solutions of polymers (e.g., polyelectrolytes) with complementary noncovalent interactions, such as electrostatic and H-bonding interactions. Polymer complexes have been extensively investigated in the forms of precipitates, coacervates and colloids for decades. However, processing of polymer complexes into bulk plastic-like polymeric materials was rarely reported, because polymer complexes were generally thought to be unprocessable. Schlenoff and coworkers reported the processing of polyelectrolyte complexes with a regular extruder by adding salts into the system to break the electrostatic interactions between the polyelectrolytes, resulting in plastic-like materials with true stress at break of several megapascals. Recently, our group developed a different strategy, involving precipitation and compression molding procedures, to process various kinds of polymer complexes into plastic materials with tailored microstructures and outstanding mechanical properties. We reported a mechanically super-strong and healable polymer composite as a plastic material derived from the polymer complexes of polyacrylic acid (PAA) and polyvinylpyrrolidone (PVPON) crosslinked by H-bonds. After mixing the aqueous solutions of PAA and PVPON, the resultant precipitates of the H-bonded complexes can be processed into desired shapes via the compression molding method. A plastic material was finally obtained after the sample was dried (Figure 2a,b). When the monomer molar ratio between PAA and PVPON in the resultant PAA–PVPON composite reaches 0.98:1.0 (denoted as PAA$_{0.98}$–PVPON$_{1}$), the PAA$_{0.98}$–PVPON$_{1}$ composite exhibits a well-defined phase-separated nanostructure. Transmission electron microscope (TEM) measurements of the stained PAA$_{0.98}$–PVPON$_{1}$ sample show that uniform spherical PAA–PVPON nanoparticles with diameters of ∼37 nm are homogeneously dispersed in the matrix of the polymer composite (Figure 2C). Compared with the PAA–PVPON complexes with other compositions, the PAA$_{0.98}$–PVPON$_{1}$ composite has the highest density of PAA–PVPON nanoparticles with the narrowest size distribution. As a result, the PAA$_{0.98}$–PVPON$_{1}$ composite exhibits the highest tensile strength of ∼81.1 MPa among all the prepared PAA–PVPON composites and a very high stiffness with a Young’s modulus of ∼4.5 GPa (Figure 2D, Table 1). Systematic investigation indicates that the nanoparticles shown in the TEM image mainly consist of PAA–PVPON complexes with core-shell structures, wherein the core is highly aggregated PVPON and the shell is highly crosslinked H-bonded PAA–PVPON complexes (Figure 2E). The aggregation of PVPON results from the hydrophobic interactions between the pyrrolidone groups, leading to the formation of core-shell structures of the PAA–PVPON complexes. The exceptionally high mechanical performance of the PAA$_{0.98}$–PVPON$_{1}$ composite not only originates from the high density of H-bonds between the two polymers, but also benefits from the reinforcement effect of the PAA–PVPON nanoparticles. The PAA–PVPON nanoparticles serve as homogeneously dispersed “hard” nanofillers that have strong interfacial interactions with the matrix of the PAA–PVPON complexes, further cross-linking the polymer chains in the matrix to effectively reinforce the PAA$_{0.98}$–PVPON$_{1}$ composite. Controlled experiments were conducted to prepare the PAA–PVPON composites in ethanol instead of aqueous solutions. The resultant PAA–PVPON composites exhibit featureless nanostructures without nanoparticles observed under TEM, while the as-obtained materials are quite brittle with much inferior mechanical performances. Thanks to the reversibility of the H-bonds between PAA and PVPON, the mechanically super-strong PAA$_{0.98}$–PVPON$_{1}$ composite is self-healable to restore its original
mechanical performance, even after break, after 11 h of immersion in water of ∼45°C followed by incubation in air for ∼18 h. (Figure 2F). Based on the complexation of PAA and poly(allylamine hydrochloride) (PAH) (Figure 2G), our group also fabricated a mechanically strong and highly stiff plastic material of PAA–PAH composite via the similar preparation method. The electrostatic and H-bonding interactions between PAA and PAH were exquisitely regulated by changing their ratios and the pH of the PAA–PAH mixture solutions. Because of the incompatibility between the electrostatic and H-bonded PAA–PAH complexes, the PAA_{1.6}–PAH_{1.0} composite (PAA:PAH monomer molar ratio is 1.6:1.0) exhibits a well-defined phase-separated nanosstructure (Figure 2H). The phase of H-bonded PAA–PAH complexes, existed as nanospheres, are homogeneously dispersed in the continuous phase that mainly consists of the electrostatic PAA–PAH complexes. Such a phase-separated structure endows the PAA_{1.6}–PAH_{1.0} composite with a double cross-linked feature, wherein the homogeneously dispersed nanospheres act as crosslinkers and nanofillers to significantly reinforce the material (Figure 2I). As a result, the PAA_{1.6}–PAH_{1.0} composite exhibits a very high tensile strength and Young’s modulus of ∼67 MPa and ∼2.0 GPa (Table 1), respectively, which are much higher than those
of other PAA–PAH composites without the phase-separated nanostructure (e.g., PAA₁.₀–PAH₁.₀ composite with tensile strength of ~47 MPa and Young’s modulus of ~1.2 GPa). Furthermore, the fractured PAA₁.₆–PAH₁.₀ composite can be readily healed at the ambient condition by using the liquid-like form of the PAA–PAH complexes (i.e., PAA–PAH coacervate) as an intermediary healing agent (Figure 2J).

Enhancement of the mechanical performances of commercial plastics is a long-standing pursuit, it is however quite challenging to homogeneously disperse nanofillers in commercial thermoplastics.[72–76] Aiming at the reinforcement of commercial thermoplastics, our group has developed an effective strategy of polysulfones, a family of tough thermoplastics with high thermostability, by complexing carboxylic acid-functionalized poly(aryl ether sulfone) (PAES-COOH) with a small fraction of PVPON.[48] PAES-COOH/PVPON complexes that are well dispersed in the polymer complexes. The in situ formed aggregates work as additional crosslinking domains and “hard” nanofillers of the polymer matrix to significantly reinforce the polymeric materials.

There are also some examples reported by other groups, demonstrating the reinforcement of commercial polymeric materials via the in situ formed noncovalent aggregates.[62,63] Song and coworkers developed a highly strong and super-tough plastic film by complexing deformable granules and polyvinyl alcohol (PVA) through multiple H-bonding interactions between the different blocks. PV A–HA–Fe 120.1 4.7 27.4 N/R [50]

TABLE 1 Summary of the mechanical properties of each sample described in this article, wherein “N/R” represents “not reported”

| Samples | Tensile strength (MPa) | Young’s modulus (MPa) | Elongation at break (%) | Toughness (MJ m⁻³, if not specified) | Ref. |
|---------|------------------------|-----------------------|-------------------------|-------------------------------------|------|
| Plastics |                        |                       |                         |                                     |      |
| PAA₀.₉₈–PVPON₁ | 81.1                   | 4.5                   | 2.1                     | N/R                                 | [46] |
| PAA₁.₀–PAH₁.₀ | 67.2                   | 2.0                   | 2.8                     | 1.21                                 | [47] |
| PAES-COOH/PVPON₁₉% | 104.8                 | 0.93                  | 16.2                    | N/R                                 | [48] |
| PVA/10 wt% SSEBS | 91.2                   | 1.85                  | 205                     | 122 J g⁻¹                            | [62] |
| TA-PVA₄₅ | 104.2                  | 3.53                  | 404.7                   | 395.2                                | [49] |
| VPVA–HA–Fe | 120.1                  | 4.7                   | 27.4                    | N/R                                 | [50] |
| Elastomers |                        |                       |                         |                                     |      |
| HBP-3 | 3.8                    | 35.7                  | 310                     | N/R                                 | [104] |
| PEG–CAT–Fe | 21.9                   | 184                   | 170                     | 22                                  | [105] |
| PT-HM-U20 | 44                     | 5.8                   | 2580                    | 345                                 | [106] |
| PU-BPY₉.₅–Zn | 52.4                   | N/R                   | 2250                    | 363.8                                | [51] |
| IPDI-SPU₂₀₀₀ | 75.6                   | 8.3                   | 1520                    | 390.2                                | [52] |
| Hydrogels |                        |                       |                         |                                     |      |
| (PDDA/PEI)—(PSS/PAA) | 1.26                  | 0.36                  | 2434.2                  | 19.53                                | [53] |
| PAA–PEI–PY₉.₁₆% | 1.1                    | 0.34                  | 2970                    | 18.2                                 | [54] |
| DMAA–co–MAAc | 1.6                    | 28                    | 450                     | 9.3 kJ m⁻²                           | [5]  |
| PE₉₀₁₃/A₆₆/MPEG₀₄ | 4.7                    | N/R                   | 1200                    | 32.6                                 | [55] |
| PVA–CB₉₀₁₂ | 5.8                    | N/R                   | 500                     | 14.9                                 | [56] |

| Samples | Tensile strength (MPa) | Young’s modulus (MPa) | Elongation at break (%) | Toughness (MJ m⁻³, if not specified) | Ref. |
|---------|------------------------|-----------------------|-------------------------|-------------------------------------|------|
| Samples |                        |                       |                         |                                     |      |
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| TA-PVA₄₅ | 104.2                  | 3.53                  | 404.7                   | 395.2                                | [49] |
| VPVA–HA–Fe | 120.1                  | 4.7                   | 27.4                    | N/R                                 | [50] |
mechanical strength of the PVA/SSEBS composite. On the other hand, the deformable SSEBS nanoparticles can effectively dissipate energy under external force, significantly improving the extensibility and toughness of the PVA/SSEBS composite. The as-developed PVA/10 wt% SSEBS film exhibits a very high tensile strength of ∼91.2 MPa, a Young’s modulus of ∼1.85 GPa and a large elongation-at-break of 205%, resulting in an exceptional specific toughness of ∼122 J g⁻¹. The toughness is 7.06 times higher than that of the pure PVA film prepared at the same condition.

The PVA-based polymeric films with enhanced mechanical performances have been extensively developed by incorporation of various kinds of nanofillers based on the solution casting method. Nevertheless, large-scale production of processable PVA-based bulk plastics is highly desirable, considering that the thermal processing of PVA is a big challenge worldwide because the melting point of PVA is very close to its decomposition temperature. Our group has developed a processable, degradable, healable, and recyclable PVA-TA (tannic acid) composite plastic that combines superhigh strength and ultra-high toughness. The PVA-TA composite can be fabricated and processed into different shapes via the solution mixing and compression molding processes (Figure 3A–C). The resultant PVA-TA composite consists of interpenetrating three-dimensional supramolecular PVA-TA clusters, which are formed because of the H-bonded aggregation of PVA chains into the dendritic TA molecules (Figure 3D). On one hand, the densely cross-linked and highly confined PVA chains by the PVA-TA clusters can effectively restrain the mobility of PVA chains to strengthen and stiffen the PVA-TA composite. On the other hand, the high-density H-bonds in the PVA-TA clusters can synergistically break and reform upon load to effectively dissipate energy, endowing the PVA-TA composite with high extensibility and toughness. Consequently, the as-developed PVA-TA composite exhibits a super-high tensile strength of ∼104.2 MPa in combination with an ultrahigh specific toughness of ca. 282.3 J g⁻¹ (395.2 MJ m⁻³) and a Young’s modulus as high as ∼3.53 GPa (Figure 3E, Table 1). The toughness is even higher than that of the toughest spider silk (ca. 354 MJ m⁻³) ever found in the world, while the tensile strength is higher than that of most engineering plastics (Figure 3F). Moreover, the PVA-TA composite can be degraded into nontoxic species in soil due to the dissociation of the H-bonded PVA and TA. Importantly, the superstrong and ultratough PVA-TA composite is also healable after break, and recyclable for multiple generations, at room temperature, by the assistance of water to activate the reversibility of the H-bonds. Due to the high hydrophilicity of PVA, PVA-based plastics easily absorb water from the environment and generally exhibit lower mechanical strength compared to that of polyethylene-based plastics in watery environments. We have also fabricated a degradable PVA-based supramolecular plastic with high mechanical strength even in watery environments by the complexation of vanillin-grafted PVA (VPVA), hydrophobic humic acid (HA), and Fe³⁺ ions (VPVA–HA–Fe complexes). Large-area VPVA–HA–Fe plastics can be easily prepared from the solution of VPVA–HA–Fe complexes using a blade-coating method. The strong coordination interactions between Fe³⁺ ions and HA leads to aggregation of HA, forming Fe³⁺-chelated HA nanoparticles that are homogeneously dispersed in the H-bonded VPVA-HA matrix (Figure 3G,H). The in situ formed Fe³⁺-chelated HA nanoparticles serve as the crosslinkers and nanofillers of the polymer network, significantly strengthening and stiffening the VPVA–HA–Fe plastic. The yielding strength, breaking strength, and Young’s modulus of the VPVA–HA–Fe plastics reach ∼120.1 MPa, ∼85.0 MPa, and ∼4.7 GPa (Figure 3I, Table 1), respectively, which are all much higher than those of the VPVA plastic (∼90.7 MPa, ∼48.2 MPa, and ∼3.6 GPa). Importantly, the VPVA–HA–Fe plastic can still maintain a high breaking strength of ∼26.2 MPa even after being immersed in water at room temperature for 7 days (Figure 3I). Benefiting from the reversibility of the coordination and H-bonding interactions, the VPVA–HA–Fe plastics are recyclable and can be conveniently processed into plastic products with desired shapes (Figure 3K,L). The VPVA–HA–Fe plastics can also be completely degraded in soil into nontoxic species without requiring manual interference (Figure 3M). Overall, thanks to the outstanding mechanical performance, healability, recyclability, and degradability, the as-developed PVA-TA and VPVA–HA–Fe plastics show high promise as sustainable substitutes for conventional plastics in many applications.

Elastomers

Elastomers, including natural and synthetic rubbers, are compliant, deformable, and elastic polymeric materials that can restore their original shape after undergoing high deformation (e.g., >100%). Because of their high deformability and elasticity, elastomers have extensive applications in tires, seals, adhesives, damping, and insulating elements, and so forth. Elastomers are composed of soft and flexible polymer chains held together by intermolecular crosslinks. Highly deformable elastomers that combine high mechanical strength with high toughness are highly desirable in high-tech industries and the emerging fields such as soft robotics, actuators, and stretchable electronics. It is however a longstanding challenge to endow elastomers with high mechanical strength in combination with large deformability and high toughness. Enhancement of the mechanical strength of elastomers relies on higher-degree crosslinking of the polymer chains, while incorporation of external nanofillers is also an effective strategy in this aspect. However, higher degree of crosslinking and incorporation of nanofillers will generally suppress the deformability and toughness of elastomers. Similar to the covalent crosslinking, noncovalent aggregates of polymer chains can also serve as the crosslinkers for elastomers. Different from covalent bonds, noncovalent bonds exhibit favorable reversibility and thus can be dynamically ruptured and reformed to dissipate energy. Therefore, employment of noncovalent aggregates as the dynamic crosslinkers is an effective strategy to simultaneously strengthen and toughen elastomers. Furthermore, noncovalent crosslinking also favors the development of healable and recyclable elastomers, which can play a pivotal role in building a sustainable society due to the huge consumption of elastomers worldwide. In this part, we will summarize some typical examples of elastomers reinforced by the noncovalent aggregates of polymer chains.

Guan and coworkers developed a self-healing elastomer strengthened by the microphase-separated nanostructure,
which was derived from the self-assembly of a brush copolymer comprising a polystyrene (PS) backbone and polyacrylate amide (PA) brushes (Figure 4A).\textsuperscript{104} Such an amphiphilic copolymer undergoes self-assembly in a polar solvent, leading to the phase separation between the PS and PA segments. The PS segments are aggregated to form “hard” spherical nanodomains that are homogeneously dispersed into the “soft” matrix composed of the H-bonded PA chains (Figure 4A,B). The spherical nanoaggregates of the PS segments not only serve as physical crosslinkers of the PA chains to endow the material with elasticity, but also effectively enhance the mechanical strength and Young’s modulus of the elastomer. The tensile strength and Young’s modulus of the elastomers increase but the deformability decreases with the increase of the styrene weight fraction in the PS-PA brush copolymer (Figure 4C). Comparatively, the control samples without the phase-separated nanostructures are either very weak elastomers or exhibit little elasticity. Therefore, the mechanical performances of the elastomers are strongly dependent on their two-phase structures that can be tailored by the composition of the PS–PA copolymer. Favorably, the as-developed elastomer (HBP-3) with a tensile
strength of $\sim 3.8$ MPa and Young’s modulus of $\sim 35.7$ MPa can be self-healed autonomously at the ambient condition, thanks to the reversibility of the H-bonds between the PA chains (Figure 4C, Table 1). Apart from only strengthening/stiffening elastomers, simultaneous enhancement of their strength/stiffness and toughness is more challenging because there is always a trade-off between the strength/stiffness and deformability for elastomers.[102] Valentine and coworkers circumvented this trade-off by crosslinking the flexible poly(ethylene glycol) chains via the ionomeric iron-catechol aggregates (Figure 4D).[105] The iron-catechol aggregates exist as the chain-restricting nanodomains composed of the
reversible iron-catecholate complexes (PEG-CAT-Fe) (Figure 4E). Such a structural characteristic can not only significantly increase the crosslinking density of the polymer network, but also effectively dissipate energy due to the reversible break and reformation of the iron-catechol coordination bonds. Consequently, the PEG–CAT–Fe elastomer involving the iron-catechol aggregates shows 58-fold and 770-fold increase in tensile strength (from 0.378 to 21.9 MPa) and Young’s modulus (from 0.24 to 184 MPa), respectively, while the deformability is not sacrificed compared to the counterpart material without the iron-catechol crosslinking (Figure 4F, Table 1). As a result, the toughness of the PEG–CAT–Fe elastomer is also significantly increased by a factor of 92 (from 0.244 to 22 MJ m$^{-2}$) (Figure 4F, Table 1).

The step-growth polymerization based on the reaction between isocyanates and hydroxyl-/amine-terminated species (e.g., polymers and small-molecule chain extenders) has been extensively used for the synthesis of polyurethane/polyurea elastomers.$[51,52,106–114]$ The polyurethane/polyurea elastomers generally exhibit two-phase structures consisting of hard and soft domains. The hard domains originate from the spontaneous aggregation of urethane/urea groups due to the H-bonding interactions, while the soft domains originate from the flexible hydroxyl-/amine-terminated polymers (e.g., polyether and polyester). The hard domains serve as crosslinkers of the flexible polymer chains, endowing the polyurethane/polyurea materials with elasticity. Engineering the molecular structures of the isocyanates and chain extenders can result in hard segments with a wide variety of structures in the resultant polyurethane/polyurea polymers. The mechanical performances of the polyurethane/polyurea elastomers can thus be regulated by the structures of the hard segments. Furthermore, the polyurethane/polyurea elastomers involving mere noncovalent crosslinking are generally self-healable and/or recyclable because of the reversibility of the noncovalent bonds. In recent years, extensive progress has been made in the development of healable and/or recyclable polyurethane/polyurea elastomers with differently structured hard segments.$[51,52,106–114]$ Unfortunately, in most cases, polyurethane/polyurea elastomers involving mere noncovalent crosslinking exhibit limited mechanical strength (e.g., tensile strength < 15 MPa), though highly deformable ones have been widely reported. Li and coworkers developed a highly strong and tough healable polyurethane elastomer by incorporating urethane, urea, and 2-ureido-4[1H]pyrimidinone (UPy) groups into the hard segments.$[106]$ Such a structural design results in highly dense H-bonding interactions between the hard segments that will aggregate to form dynamic hard domains with hierarchical H-bonds. As a result, the as-developed polyurethane elastomer (PT-HM-U20) exhibits a high tensile strength of 44 MPa and a high toughness up to 345 MJ m$^{-3}$ (Table 1), while the elastomer is also healable even after break to recover its mechanical performance at elevated temperatures (e.g., 80°C for 48 h).

Apart from strengthening and toughening the elastomers, it is also highly desirable to endow them with high crack tolerance that can effectively prevent the crack propagation, even if crack or cut exists. Therefore, impartation of high crack tolerance to intrinsically robust elastomers can significantly enhance their reliability even if they are predamaged, while healability and recyclability can further extend their service life and lifecycle. However, it is extremely challenging to endow healable/recyclable elastomers with integrated high mechanical strength and toughness in combination with excellent crack tolerance. These favorable merits originate from different molecular mechanisms and thus they are generally mutually exclusive. To reconcile the tradeoffs between mechanical strength, toughness, crack tolerance, and healability/recyclability of elastomers, our group recently reported a sophisticated design of the noncovalent hard domain of a polyurethane elastomer.$[111]$ We synthesized a multiblock polyurethane polymer comprising flexible polydimethylsiloxane (PDMS) chains, crystallizable poly-caprolactone (PCL) chains, bipyridine groups, and carboxylate groups (Figure 5A,B). The aggregation of different segments, including the bipyridine groups coordinated with Zn$^{2+}$ ions, carboxylate groups cross-linked by H-bonds, and crystallization of the PCL chains, leads to the formation of dynamic hierarchical hard domains in the polyurethane elastomer (denoted as PU-BPY-Zn) with a phase-separated structure (Figure 5C). The hierarchical hard domains serve as rigid nanofillers to significantly strengthen the elastomer, while the hard domains are also deformable and capable of disintegrating upon a high external force. The disintegration of the hierarchical hard domains can release the hidden length of the polymer chains to significantly increase the elongation and toughness of the elastomer. Furthermore, the PCL segments in the hard domains can slip along the stretching direction to further crystallize during deformation and disintegration of the hierarchical hard domains. The newly generated PCL nanocrystals further increase the energy barrier for the rupture of the elastomers. As a result, rupture of the sacrificial bonds, disintegration of the hierarchical domains, and stress-induced crystallization of the PCL chains cooperatively enhance the toughness and damage tolerance of the as-developed PU-BPY-Zn elastomers. The distinctive strengthening and toughening effect of the hierarchical hard domains makes the PU-BPY-Zn elastomer exhibit a very high tensile strength of ~52.4 MPa, an enormous toughness of ~363.8 MJ m$^{-2}$, and unprecedented crack tolerance with fracture energy as high as ~192.9 J m$^{-2}$ (Figure 5D,E, Table 1). Remarkably, the fracture energy even exceeds that of Zn alloys and Ti alloys.$[115]$ Furthermore, the PU-BPY-Zn elastomer can be healed with the healing efficiency of nearly 100% at 100°C for 3 h, while the elastomer can also be recycled without altering its original mechanical properties by dissolving the samples in tetrahydrofuran followed by a cast procedure (Figure 5D).

To simplify the fabrication of highly strong, tough, and crack-tolerant elastomers, we have made meticulous molecular engineering of the linear poly(urethane-urea) polymer for the development of a supramolecular elastomer with record high mechanical robustness and crack tolerance, by mimicking the unique H-bond arrays in spider silk.$[152]$ The H-bonding segment of the linear poly(urethane-urea) polymer is meticulously engineered to comprise abundant H-bond donors and acceptors by the construction of multiple acyclic hexatomic spacers with higher flexibility, instead of the rigid aromatic spacers (Figure 6A). Importantly, the ASCZ and urethane moieties are linked by the alicyclic hexatomic spacers with higher flexibility, instead of the rigid aromatic spacers (Figure 6A). Aggregation of the alicyclic H-bonding segment favors the formation of higher density of distinctive hard domains (i.e., H-bond arrays) that exhibit smaller sizes but involve
denser H-bonds in the resultant IPDI-SPU2000 elastomer, compared to TDI-SPU2000 elastomer bearing the aromatic H-bonding segment (Figure 6B). Similar to the strengthening and toughening mechanism of spider silk,[84] the hydrogen-bond arrays act as firm but reversible crosslinks and sacrificial bonds for enormous energy dissipation, conferring exceptional mechanical robustness, extremely high crack tolerance, healability and recyclability on the elastomer. The as-developed IPDI-SPU2000 elastomer has the highest tensile strength of 75.6 MPa ever recorded for polymeric elastomers (Figure 6C,D, Table 1), and exhibits a true stress at break as high as \( \sim 1.21 \text{ GPa} \) that is comparable to that of typical spider silk (Figure 6D,E). Meanwhile, the IPDI-SPU2000 elastomer possesses an enormous toughness of \( \sim 390.2 \text{ MJ m}^{-3} \), which is \( \sim 2.4 \) times higher than that of typical spider silk (Figure 6D,E, Table 1).[84] The combination of such high strength and toughness renders the IPDI-SPU2000 elastomer the strongest and toughest healable elastomer thus far (Figure 6D). Thanks to the effective energy dissipation capability, the IPDI-SPU2000 elastomer shows superb crack tolerance (Figure 6F) with an unprecedentedly high fracture energy of \( \sim 215.2 \text{ kJ m}^{-2} \), which is even greater than that of metals and alloys.[115] The exceptionally robust and crack-tolerant IPDI-SPU2000 elastomer show promising prospect in high-tech industries, such as the aerospace and defense industry, as an exceedingly reliable and durable materials for loadbearing and energy-absorbing applications. The IPDI-SPU2000 elastomer also exhibits healability at 100°C for 36 h and recyclability realized by hot pressing at 130°C and 5 MPa for 0.5 h (Figure 6G,H), making the elastomers a highly sustainable material for the emerging applications such as soft robotics, flexible electronics, and stretchable optical devices.

### Hydrogels

Hydrogels are three-dimensional polymer networks that encapsulate a large amount of water in between the chemically and/or physically cross-linked polymer chains. Hydrogels have drawn great attention as the equivalents of biological tissues for a variety of biomedical applications, such as tissue engineering, drug delivery, wound dressing, and so forth.[116–121] The high variability of the mechanical properties makes hydrogels appealing for different applications. Conventional hydrogels are generally too weak or brittle for the real-world use. Similar to the reinforcement of plastics and elastomers, hydrogels can also be reinforced by either intrinsically increase the crosslinking density of polymer chains or extrinsically incorporating external nanofillers.[153–156,122–125] In these aspects, double-network crosslinking and incorporation of inorganic/organic nanofillers are typical strategies to enhance the mechanical...
properties of hydrogels.\textsuperscript{[36–38,124–127,129]} Recently, our group developed different methodologies for the fabrication of distinctive hydrogels with in situ formed noncovalent aggregates.\textsuperscript{[53–56]} The noncovalent aggregates in hydrogels serve as both crosslinkers and well-dispersed nanofillers of the polymer networks, playing a significant role in reinforcing the hydrogels. The aggregates can be well tailored with respect to their sizes, distribution, and dispersion, facilitating the variation and optimization of the mechanical properties of the hydrogels. Furthermore, the noncovalent interactions between the polymer chains can also endow the hydrogels with healability and recyclability.

Our group has developed a strategy of noncovalent complexation of complementary polymers for the fabrication of hydrogels with phase-separated structures.\textsuperscript{[53–56]} Regulation of the components, intermolecular interactions, and experimental parameters of the polymer complexation can result in hydrogels with tailored phase-separated structures that play a significant role in strengthening and toughening the hydrogels. A two-phase-structured hydrogel composed of four polyelectrolytes, termed as the (PDDA/PEI)-(PSS/PAA) hydrogel, was fabricated by mixing a positively charged polyelectrolyte mixture of poly(diallyldimethylammonium chloride) (PDDA)/PEI with a negatively charged polyelectrolyte mixture of poly(sodium 4-styrenesulfonate) (PSS)/PAA in an aqueous solution, followed by molding, drying, and rehydration (Figure 7A,B).\textsuperscript{[53]} During the complexation of the four polyelectrolytes, the incompatible association between the strong (PDDA and PSS) and week (PEI and PAA) polyelectrolytes leads to the in situ formation of PDDA-PSS nanoparticles dispersed in the PEI-PAA matrix (Figure 7C,D). The size, distribution and dispersion of the PDDA-PSS nanoparticles can be tailored by the relative contents of the four components. The PDDA-PSS nanoparticles, exhibiting more uniform size distribution and more homogeneous dispersion in the PEI-PAA matrix, will benefit the reinforcement of the (PDDA/PEI)-(PSS/PAA) hydrogel. This is similar to the phenomenon and mechanism
of the reinforcement of polymer composite via inorganic nanofillers. The PDDA-PSS nanoparticles not only act as stiff nanofillers associated strongly with the PEI-PAA matrix to strengthen the hydrogel, but also serve as deformable energy-absorbing crosslinkers to effectively dissipate energy and thus toughen the hydrogel. The tensile strength, elongation-at-break, and toughness of the optimal (PDDA/PEI)-(PSS/PAA) hydrogel are ~1.26 MPa, ~2434.2%, and ~19.53 MJ m$^{-3}$, respectively, which are 2.4, 1.8, and 5.2 times higher than the corresponding values of the PEI-PAA hydrogel without the phase-separated structure (Figure 7E, Table 1). The (PDDA/PEI)-(PSS/PAA) hydrogels are healable in water with the healing efficiency of ~95% for the tensile strength and ~100% for the elongation-at-break (Figure 7F,G). The hydrogels can also be recycled by drying and grinding the samples, followed by a compression molding process in the presence of water (Figure 7H). Homogeneous incorporation of stiff inorganic or organic nanofillers into hydrogels is the widely employed strategy to reinforce hydrogels.\cite{122,124-128,130} However, the hydrogels strengthened by the external nanofillers usually exhibit decreased extensibility because of the restrained polymer chain mobility exerted by the nanofillers. Our group reported the simultaneous enhancement of mechanical strength and extensibility of the polyelectrolyte-based hydrogels via the in situ formed nanofibril aggregates derived from the self-assembly of organic molecules.\cite{54} Complexation of PAA with the complexes of branched PEI and
1-pyrenylbutyric acid (PEI-PYA) results in the PAA–PEI–PYA complexes, which were further molded, dried and then rehydrated to generate the PAA–PEI–PYA hydrogel (Figure 7I). The PYA molecules electrostatically associated with the PEI chains undergo self-assembly during the further complexation with PAA, leading to the formation of nanofibril crystals in the final PAA–PEI–PYA hydrogel (Figure 7I). On one hand, the mechanical strength of the PAA–PEI–PYA hydrogel can be significantly enhanced by the rigid PYA nanofibrils. One the other hand, effective energy dissipation can be achieved by the force-induced sliding of the PYA nanofibrils and the reversible breakage of H-bonding and electrostatic interactions among PAA, PEI, and PYA nanofibrils. In this scenario, both the mechanical strength and extensibility of the PAA–PEI–PYA hydrogels are simultaneously enhanced, as compared to the PAA–PEI hydrogel without the PYA aggregates. The PAA–PEI–PYA$_{2.1\%}$ hydrogel (mass fraction of PYA is 2.1%) exhibits the optimal mechanical performance with a tensile strength of $\sim$1.13 MPa, elongation-at-break of $\sim$2970%, and toughness of $\sim$18.17 MJ m$^{-3}$, which are 2.2, 2.1, and 4.8 times higher than those of the PAA/PEI hydrogels, respectively (Figure 7I, Table 1). The PAA–PEI–PYA hydrogels are also healable and recyclable thanks to the reversible H-bonds and electrostatic interactions between the components (Figure 7K).

Other strategies have also been reported for the fabrication of hydrogels with polymer-rich aggregates stabilized by the hydrophobic interactions. Sheiko and coworkers reported the one-pot synthesis of a highly stiff hydrogel via the free-radical copolymerization of N,N-dimethylacrylamide (DMAA) and methacrylic acid (MAAc) in water (Figure 8A).$^{[5]}$ During the copolymerization of DMAA and MAAc, association between the DMAA and MAAc units due to the H-bonding interactions leads to the formation of polymer-rich aggregates stabilized by the hydrophobic interactions originated from the presence of the $\alpha$-methyl groups of poly(methacrylic acid) (PMAA) (Figure 8A,B). The resulted hydrogel (DMAA-co-MAAc) is composed of a composite network in which the H-bonded polymer-rich aggregates are imbedded in a loose covalent network (Figure 8A,B). Through systematically varying the water fraction, monomer composition, and initiator concentration, the size, distribution and density of the polymer-rich aggregates can be well regulated, leading to the formation of bimodal distribution of particles sizes, centered at 70 ± 30 nm and 250 ± 70 nm in diameter. Larger and more rigid aggregates sustain larger macroscopic strain, while smaller and weaker clusters lead to energy dissipation during deformation. Consequently, the mechanical properties of the as-synthesized hydrogels can be tuned by varying the experimental parameters. The optimized hydrogel with the highest density of nanoparticles has a Young’s modulus as high as 28 MPa, a tensile stress of 1.6 MPa, and a toughness of 9.3 kJ m$^{-2}$ (Figure 8C, Table 1). Controlled experiments were conducted to fabricate the hydrogels based on the copolymerization of DMAA and acrylic acid (AAc) without the $\alpha$-methyl groups, resulting in quite soft and weaker DMAA-co-AAc hydrogels. Therefore, the significantly enhanced stiffness of the DMAA-co-MAAc hydrogel is attributed to the enhancement effect of the hydrogen-bonded aggregates mediated by hydrophobic interactions. The reliability and durability of hydrogels not only depend on their mechanical robustness, but also rely on their elastic self-recovery ability because excellent self-recovery can endow the hydrogel with fatigue resistance upon long-term use and repeated deformation. Through one-step polymerization of acrylic acid (AA) and poly(ethylene glycol) methacrylate (MPEG) in the presence of the oppositely charged PEI, our group also developed a two-phase-structured hydrogel with combined high tensile strength, high toughness, and excellent elastic self-recovery ability (Figure 8D).$^{[53]}$ During the polymerization process, insoluble PAA/PEI complexes can be in situ formed in the resultant PEI/AA/MPEG hydrogels (Figure 8E). As such, PEI/AA/MPEG hydrogels with two-phase structures were obtained, wherein the PAA/PEI nanoparticles are homogeneously dispersed in the hydrogels (Figure 8E). The sizes and distribution of the PAA/PEI nanoparticles can be tuned by changing the relative fractions of the three components to optimize the mechanical properties of the PEI/AA/MPEG hydrogels. The PAA/PEI nanoparticles, in situ formed during the copolymerization of AA and MPEG, have strong affinity and high compatibility with the polymer matrix of the hydrogel. The PAA/PEI nanoparticles work as “hard” and firm crosslinking domains of the polymer matrix to significantly reinforce the hydrogel and endow the hydrogel with excellent elastic self-recovery ability. As a result, the optimized PEI/AA/MPEG hydrogel exhibits a high tensile strength of $\sim$4.7 MPa and a large elongation-at-break of $\sim$1200% (Figure 8F, Table 1). Moreover, the hydrogel can quickly recover from a $\sim$300% strain to its original length within 10 min at room temperature without any external assistance (Figure 8G). Furthermore, the PEI/AA/MPEG hydrogel after break can be healed at the healing efficiency of $\sim$42.5% for tensile strength by immersing the samples in a NaCl solution (Figure 8H).

It is always challenging to reconcile the unfavorable trade-off between the mechanical robustness and healing capability for healable materials.$^{[127,128]}$ To circumvent this problem for hydrogels, it is envisioned that impartation of dynamic properties to the in situ formed noncovalent aggregates can simultaneously reinforce the hydrogels and improve their healing capability. Accordingly, we designed a PVA-based polymer by grafting 4-carboxybenzaldehyde (CBA) onto the PVA chains (Figure 8I).$^{[56]}$ Sequential dialysis of the DMSO solution of PVA–CBA into ethanol and water results in the formation of the PVA–CBA hydrogel with a phase-separated structure (Figure 8I). During the dialysis process, the hydrophobic interactions lead to the spontaneous aggregation of the CBA groups, resulting in the in situ formed hydrophobic domains in which the PVA–CBA chains are further cross-linked by the H-bonds between the hydroxyl groups and the H-bonds between the hydroxyl and carboxylic acid groups (Figure 8I). The hydrophobic domains act as crosslinkers and deformable nanofillets, significantly enhancing the mechanical strength and toughness of the PVA–CBA hydrogel. The as-developed PVA–CBA$_{0.12}$ (feed molar ratio of CBA to PVA is 0.12) hydrogel exhibits a tensile strength up to $\sim$5.8 MPa and a toughness up to $\sim$14.9 MJ m$^{-3}$, which are $\sim$5.3 and $\sim$8.7 times higher than those of the PVA hydrogel (Figure 8I, Table 1). Importantly, the in situ formed hydrophobic domains involving abundant H-bonds exhibit reversibility and thus are capable of dynamically reforming after break. The reversible and dynamic property of the hydrophobic domains enable the strong and tough PVA–CBA...
hydrogel to rapidly and efficiently heal physical damages at the ambient condition (Figure 8K). Only 1-min healing can reach a healing efficiency of 50% with respect to the tensile strength (Figure 8L), while healing for 12 h can completely restore both the tensile strength and elongation-at-break of the PVA–CBA$_{0.12}$ hydrogel. Impressively, the as-developed PVA–CBA$_{0.12}$ hydrogel with a tensile strength of $\sim$5.8 MPa and a healing efficiency of $\sim$100% at the ambient condition is the mechanically strongest self-healing hydrogel known to date (Figure 8L).

SUMMARY AND OUTLOOK

Noncovalent aggregates of biomacromolecules are ubiquitous in biological materials and systems, playing unique and vital roles in the mechanical performances and functions of biomaterials and biosystems. In artificial materials, especially the polymeric materials, noncovalent aggregates can be spontaneously formed due to the association of polymer chains driven by the noncovalent interactions between the complementary functional groups. We have highlighted in
this Review article that the in situ formed noncovalent aggregates in different polymeric materials play a key role in the enhancement of their mechanical performances. The composition, structure, dispersion, deformability, dynamic property of the in situ formed aggregates can be varied and tailored in different polymeric systems. As a result, the reinforcement of the polymeric materials is embodied in different aspects, ranging from the mere enhancement of strength to simultaneous enhancement of the strength, deformability, toughness, and elasticity. Furthermore, sophisticated design of the noncovalent aggregates can also endow the polymeric materials with exceptional damage tolerance and excellent elastic self-recovery. Moreover, the reversibility and dynamic properties of the noncovalent aggregates favor the development of healable and recyclable polymeric materials with extraordinary mechanical performances. This Review article collates the recently reported polymeric materials that are particularly reinforced by the in situ formed noncovalent aggregates, so that researchers can find inspiration for the development of high-performance polymeric materials from outside traditional strategies.

Regulation of the noncovalent aggregation of polymer chains in polymeric systems offers encouraging opportunities to develop artificial materials with mechanical performances that are comparable to or even exceed the high-performance natural materials. However, there are also challenges in understanding and characterization of the structures and dynamic properties of the spontaneously formed noncovalent aggregates at the molecular level, which is crucially important for tailoring the structures of the aggregates in a more accurate way. Moving forward, the accurate regulation of the noncovalent aggregates in polymeric systems is fundamentally necessary to elucidate the composition–structure–property relationship and design new polymeric materials with ever-higher mechanical performances. Moreover, the noncovalent bonds are generally sensitive to heat and/or other external stimuli due to their reversible and dynamic properties, while the reversibility of noncovalent bonds is favorable for the healability and recyclability of polymeric materials. Therefore, enhancement of the thermal stability of the noncovalent aggregates and attenuation of the negative effect of the noncovalent bonds on the stability of polymeric materials are also critical aspects to be addressed. Finally, beyond the enhancement of mechanical performances, the involvement of noncovalent aggregates in polymeric systems also affords a versatile avenue to functionalize the polymeric material thanks to the diversity of functional groups assembled in the aggregates. It is believed that the well-regulated noncovalent aggregation of polymer chains in polymeric materials offers an effective supplementary avenue for the development of novel polymeric materials with extraordinary mechanical performances and functionalities.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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