

Old inspires new: activation and stabilization of iodine in diene-based rubbers

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In 1920, Hermann Staudinger put forward the concept that rubber is composed of isoprene units, which has been considered as the beginning of “macromolecular science” or “polymer science.” The past 100 years’ development of polymer science has witnessed the greatness and foresight of this groundbreaking theory. On the occasion of the 100th anniversary of the birth of polymer science, this paper is dedicated to recalling a piece of research history on rubber.

Tracing the history of polymer science, rubber plays an important role in its development. Natural rubber (*cis*-1,4-polyisoprene) is one of the most important polymers, with high flexibility and elasticity. However, it did not show any viable commercial use due to the limited mechanical strength until Goodyear’s discovery of vulcanization in 1839, whereby sulfur was doped in rubber and significantly improved the mechanical strength and durability of natural rubber. This improvement sparked the rubber industry to grow dramatically at the turn of the 20th century and also encouraged the advent of the bicycle and automobile industrial age. Since then, people have never interrupted the endeavor to optimize the properties of rubbers by blending different dopants.

Other than sulfur, multiple dopants have been investigated in the modification of rubbers. Iodine aroused people’s attention in the 1980s because it proved useful in preparing conducting polymers with polyacetylene via doping. The doping of iodine in rubbers endowed nonconjugated polymers with good conductivity and enabled use of rubbers in the fields of electronics, optics, and magnetics.¹ However, this progress was mainly reported during the period from 1980 to 2000. During the 21st century few papers have

been published as more and more researchers have come to realize that the stability in conductivity of iodine-doped rubbers would attenuate with time. The instability of conductivity led to their inability in electronic, optical, and magnetic performance, which hindered the practical applications of iodine-doped rubbers. As pointed out, the loss of iodine and influence of air on the active species generated during iodine doping are supposed to be responsible for the instability of conductivity. A concept was conceived that if the active species within the iodine doping rubber could be utilized or stabilized controllably, the potential use of iodine doping materials would be achieved in broader applications.

ACTIVATION AND STABILIZATION OF IODINE

Our group has been focusing on the iodine-doping process over the past several years (Figure 1). The motivation started originally from the formulation of a processable photothermal dark material.² The photothermal materials developed focus mainly on carbon-based and metal-based materials and conjugated polymers. They are not preferable for additive manufacturing for customized production in terms of the rigidity in chemical structure or high melting point. A new type of photothermal material was demanded. Synthetic rubber, *trans*-1,4 polyisoprene (TPI), possesses a relatively low melting point and good melting processing ability. Inspired by the optically dark appearance of doped rubbers, we developed the post-darkening technique for processable photothermal materials. It manufactured

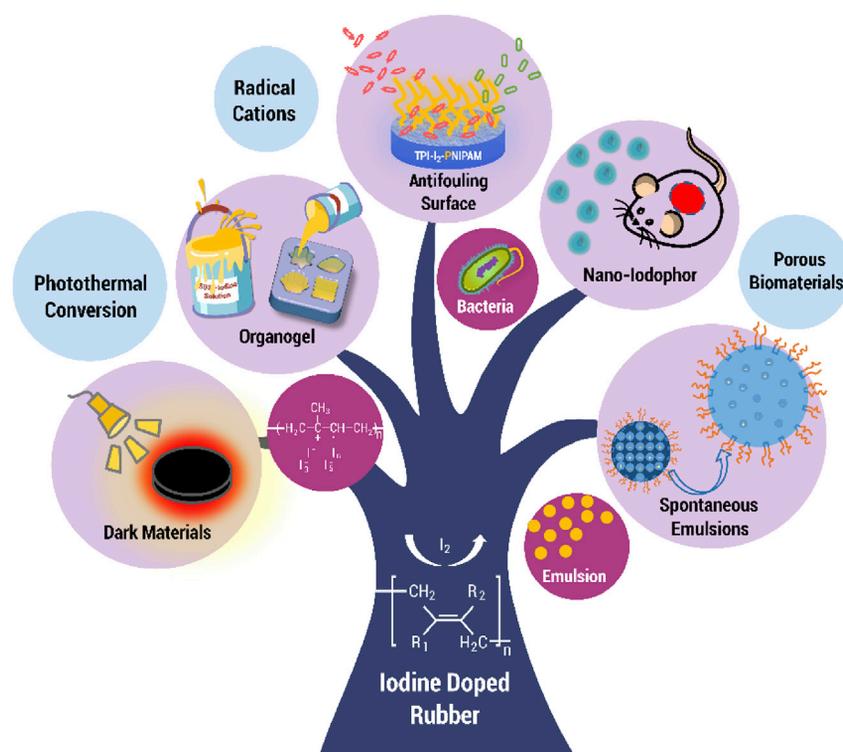


Figure 1. Iodine-doped rubber systems

TPI into any shape and size, and refreshed it into photothermal materials with 91.2% near-infrared (NIR) light photothermal conversion efficiency via iodine doping. Most notably, the photothermal conversion ability only slightly decreased after placing the materials in air without any protection for 6 months. This observation demonstrated that the photothermal conversion ability is not sensitive to the loss of iodine and oxidation of oxygen. Through X-ray photoelectron spectroscopy, electron paramagnetic resonance, Raman spectroscopy, and solid nuclear magnetic resonance, an iodine-doping process and mechanism were proposed.² As shown in Figure S1, at the early stage iodine molecules form complexes with double bonds in rubber. Subsequently, redox reactions took place between iodine and double bonds, giving rise to radical cations and iodide ions. As more iodine was added, polyiodides were generated. It was confirmed that polyiodides, $I - n$ ($n = 3, 5, 7, 9, \dots$), countered by radical cations formed during iodine doping, behaved as main light absorbers and converters, which was supported by density functional theory calculation. The polymer scaffold played a critical role in maintaining the photothermal conversion ability by stabilizing the mutable iodine species. This work allowed us to have faith in the application of the iodine system in photothermal conversion. With this vision, balancing the activation and stabilization of iodine in rubber has been the focus of our research. On the one hand, the active species formed by iodine doping are expected to be applied in functionalization of the iodine-doped materials. On the other hand, the chemical environment of iodine would be controlled to stabilize the iodine species and make the best use of the features of iodine.

Specifically, the addition of iodine not only endowed rubber with photothermal conversion ability but also transformed the double bonds into radical cations and activated the reactivity of the rubber surface. The active radical cation was applied to initiate the grafting of a thermoresponsive polymer, poly(*N*-isopropylacrylamide) (PNIPAM), on the iodine-doped rubber surface, which has controllable wetting behaviors at different temperatures³ without a complicated degassing step or any other specific catalysts. The successful grafting of polymer confirmed the existence of radical cations and gave strong evidence for the assumed iodine-doping mechanism as stated above. The photothermal conversion of dark rubber can increase the surface temperature and trigger the release of iodine. Instead of being inhibited, the released iodine was used as an antibacterial agent, which has a temperature-induced and controlled release depending on the on-off switch and powers of sunlight. Combining the temperature-controlled wetting surface, a sunlight-responsive smart antifouling surface was fabricated. This work extended the application of the rubber from NIR windows to sunlight. On the other hand, it provided a new avenue of applying rubbers smartly and creatively rather than only in the traditional rubber industries.

Compared with the expectation to seal iodine in the fields of electronics and optics, utilizing the release of iodine, described here as the activation of iodine, seems more rational and feasible in terms of the features of iodine. To further apply the controllable release of iodine, its excellent antibacterial property was extended when its activity was kept within the polymer scaffold. As is known, iodine species has been proved to possess versatile skills against bacteria, such as cell wall penetration, oxidation, and substitution of microbial composition. The traditional iodophor causes oxidative damage to healthy human cells besides bacteria. The most popular iodophor, povidone iodine, also showed a severe cytotoxic effect on osteoblasts, fibroblasts, and myoblasts, according to both *in vitro* and *in vivo* studies. Fabricating the antimicrobial rubber nanocapsule-based iodophor to replace the traditional iodophor is a strategy to solve this challenge.⁴ The double bond could fasten the iodine ions and decrease the release rate of molecular iodine, which would supposedly diminish the level of toxicity in healthy tissues. The nanocapsules not only ensure the antibacterial activity at low concentration but also offer possibilities for long-term action. Furthermore, it could promote cell growth *in vitro*, and the wound-healing process was also promoted in an *in vivo* experiment. This is the first example to show the great potential of rubber in biomedicine.

Iodine doping is applicable to all rubbers containing more double bonds than TPI. In our work under study, the polystyrene-block-polybutadiene-block-polystyrene (SBS) and *cis*-1,4 polyisoprene were modified successfully via iodine doping. The good solubility in solution of SBS offered greater possibilities for processing and manufacturing that enable the solution casting and coating of iodine-doped rubbers.

The application of doped SBS was shown in our latest work. This redox reaction within the double bond and iodine was introduced into the emulsion system.⁵ Since the redox reaction would happen between the SBS and iodine and generate prodigious ions in the oil phase, this could greatly increase the osmotic pressure during the oil phase. This osmotic pressure difference would drive the water into the oil phase and form water-in-oil (W/O) emulsion during the oil phase. The polybutadiene was endowed with the radical cations. Combined with the polystyrene block, the amphiphilic block polymer acted as a surfactant to stabilize the W/O interface. With only one-step emulsification, the spontaneous emulsion was fabricated. The unstable units, the radical cations and polyiodides, were used to achieve a balance between the osmotic pressure and the Laplace pressure. Based on this technique, porous microparticles are being prepared. Considering the cell growth-promoting and antibacterial properties, it is believed that these particles will find many uses in the field of biomedical science.

CONCLUSION AND PROSPECTS

Inspired by the pioneering works mentioned above, the concept has been proved to some degree that if the active species within iodine-doped rubbers could be utilized or stabilized controllably, the potential use of iodine-doping materials would be achieved in broader applications. The outstanding performances of these formed iodine-doped rubbers have far exceeded our expectations on these systems, as well as the versatility of iodine. There are still some challenges in this area that warrant attention, for example, the evaluation and tuning of the arrangement of iodine or iodides in the rubbers. The clarification of the structure-function relationship will contribute well to the rapid development and application of these doped rubbers. More kinds of rubbers or diene-based polymers are expected to be investigated in order to systematically optimize the photothermal conversion efficiency and the antibacterial and biomedical performance of iodine-doped rubbers. In addition, applications in wider areas and scenarios, such as iodine-induced catalysis and real-life utilization of these doped rubbers, are worth exploring. All of these findings are encouraging us to invite more researchers into this area by contributing this commentary on iodine doping of rubbers. We hope that fresh blood can be added to the studies of rubbers so that the first thing that comes up when rubbers are mentioned does not involve tires.

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SUPPLEMENTAL INFORMATION

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