



Design of Nanostructured Organosiloxane-based Materials with Dynamic Functions

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Organosiloxane-based materials are widely utilized in various applications due to the high stability of Si–O–Si networks and the availability of diverse organic functionalities. Controlling the nanostructure of organosiloxanes is crucial for creating novel functional materials. This paper presents our recent research on the design of organosiloxane-based nanomaterials with photomechanical and self-healing functions.

The first topic focuses on the fabrication of photomechanical materials through the self-assembly of organosilanes functionalized with organic chromophores. By incorporating azobenzene groups, lamellar organosiloxane films demonstrated macroscopic bending and unbending motions upon UV/Vis irradiation through photoisomerization [1,2]. Additionally, photo-responsive molecular crystals were synthesized using diarylethene- and azobenzene-modified cage-type organosiloxane oligomers [3,4]. These nanohybrid materials exhibit high thermal stability and hold promise for practical applications as photoactuators.

The second topic explores self-healing organosiloxane-based nanomaterials. Lamellar siloxane-based thin films formed through self-assembly processes utilizing surfactants exhibited reversible changes in interlayer spacings in response to humidity variations [5,6]. Importantly, the film's lateral expansion upon increased humidity facilitated rapid closure of cracks with submicrometer widths. Compared to silica-based films, organosiloxane-based films demonstrated enhanced crack-healing capabilities. These findings contribute to the development of a new class of self-healing coatings.

Furthermore, we designed self-healing silicone elastomers capable of rejoining after being cut, utilizing fluoride ions as catalysts. Fluoride ions are known to catalyze the rearrangement of siloxane networks [7]. We employed fluoride-encapsulated cage germoxane as a cross-linker for polydimethylsiloxane (PDMS) to form a transparent elastomer. The Ge–O–Ge bonds within the fluoride-encapsulated cage germoxane can be cleaved in the presence of water, releasing fluoride ions. Healing of the cut gel was observed after treatment under humid conditions, attributed to the fluoride-catalyzed rearrangement of Si–O–Si networks between the cut surfaces.

References

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