Photorheological fluids of azobenzene polymers for lubrication regulation

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Abstract: Fluid viscosity is ubiquitous property and is of practical importance in intelligent fluids, industrial lubrication, and pipeline fluid transportation. Recently, there has been a surging interest in viscosity regulation. Here, we have developed a group of photorheological fluids by utilizing azobenzene polymers with a light-induced microstructure transformation. In this work, a photosensitive polymer with 4,4'-bis-hydroxyazobenzene as the main chain was designed and synthesized as a pivotal functional material. The sufficiently large structural difference under ultraviolet and near-infrared light makes it possible to regulate the viscosity of a polyethylene glycol solution. The viscosity of the photosensitive rheological fluids under ultraviolet light radiation is found to be up to 45.1% higher than that under near-infrared light radiation. To explore this intelligent lubricating technology, the friction regulation of ceramic sliding bearings was investigated utilizing photosensitive rheological fluids. Reversible friction regulation with a ratio of up to 3.77 has been achieved by the alternative irradiation of near-infrared and ultraviolet light, which can be attributed to the differences in mechanical properties and molecular structures under ultraviolet and near-infrared light according to both simulations and experiments. Such photorheological fluids will have promising applications in controllable lubrication, intelligent rheological fluids, and photosensitive dampers.

Keywords: photorheological fluids; viscosity; azobenzene polymer; lubrication

1 Introduction

The viscosity of fluids is closely tied to industrial production and daily life, such as in navigation [1, 2], pipe flows [3], mechanical lubricants [4–11], water conservancy, and biorheology [12, 13]. In particular, with the development of intelligent fluids such as electrorheological fluids [14, 15], magnetorheological fluids [16–20], pH-sensitive fluids [21], photorheological fluids [22–24], and other stimuli-responsive fluids [25, 26], these intelligent fluids are attracting extensive attention as smart fluid dampers for vehicle [27, 28], oil and gas pipeline transportation [29], in wafer surface polishing [30, 31], and friction regulation [5, 32–36]. However, some intelligent fluids have disadvantages, such as in electrochemical corrosion in electrorheological

fluids. In addition, irreversible transformation properties, high cost and environmental pollution have blocked the development of other stimuli-responsive fluids [21, 37]. As the application of intelligent fluids has increased, new kinds of liquids are urgently needed. Among all kinds of stimuli, light stimuli have a series of advantages, including convenience, cleanliness, biocompatibility, and fast response [38, 39]. The light field shows wide potential applications in intelligent materials and mechanical systems, such as for hydrophilic/hydrophobic wetting surfaces [40, 41], light-sensitive hydrogels [42], and light-induced mechanical arms [43, 44]. Therefore, light is considered an ideal outside stimulus to regulate the viscosity of photosensitive intelligent fluids.

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Recently, a class of organic photosensitive materials has aroused increasing interest on account of their significant structural differences and responsive performance. To date, great efforts have been dedicated to intelligent materials [45–47], including diarylethene, fulgide, azobenzene, spiropyran, carbon nanotubes, and graphene oxide. These photosensitive materials are widely used in flexible robots [48], liquid transportation [40], and photoforce sensors [49]. Among these external stimuli-responsive materials, azobenzene and its derivatives have attracted the most attention due to large changes in both their geometry and molecular length under ultraviolet (UV)/visible/thermal stimuli [50–53]. Azobenzene has two isomers, trans isomers (under visible/thermal/near-infrared (NIR) light) and cis isomers (under UV light). The molecular length of the cis isomer is 38.8% shorter than that of the trans isomer. Most atoms of the trans isomer are coplanar, while those of the cis isomer are noncoplanar [53, 54]. In addition, the photoisomerization of azobenzene is reversible, which makes it possible to prepare reusable photosensitive rheological fluids. Although a single azobenzene molecule has obvious structural differences between the trans isomer and cis isomer, the differences at the angstrom scale are not effective enough to influence the macroscale performance of photosensitive rheological fluids. Therefore, magnifying the differences between the cis and trans isomer is a simple and efficient way to solve the problem. A photosensitive polymer with azobenzene as the main chain is promising to satisfy these requirements. Organic photosensitive azobenzene polymers as optical switching materials provide the advantages of being green, efficient, saving and intelligent but present challenges in developing excellent photosensitive rheological fluids.

In this work, we designed a kind of photosensitive polymer by integrating 4,4'-bis-hydroxyazobenzene as a photosensitizer into a polycondensation polymer. Interestingly, the photosensitive azobenzene polymer exhibits two totally different morphologies: One conformation is a linear chain under NIR light, and the other conformation is a serrated chain under UV light. In addition, the mechanical properties, including the Young's modulus and shear modulus, are also different under UV and NIR light. The viscosity of

the photosensitive rheological fluid under UV light is up to 45.1% higher than that under NIR light. Photosensitive rheological fluids have shown obvious reversible regulation of the friction of ceramic sliding bearings. The maximum friction coefficients could be changed by approximately 3.8-fold. These results have potential applications in intelligent fluid braking, microfluid transportation, and a wide range of fields requiring external stimuli-responsive viscosity.

2 Materials and methods

2.1 Materials

Chemicals including azobenzene derivative and hexamethylenene diisocyanate were purchased from Tokyo Chemical Industry and Sinopharm Chemical Reagent Corporation. Other reactants and catalysts, such as polyglycol 200/300/400, tetrahydrofuran (THF), and Bu_2Sn dilaurate, were obtained from Aldrich. The purity of all of these reagents is AR grade.

In this work, polymer materials were synthesized to achieve photoresponsive properties via azobenzene functional groups. 4,4'-bis-hydroxyazobenzene was particularly important to realize the folding and stretching of the polymer chains corresponding to the cis isomer and trans isomer conformations. The polymer was the polycondensate of 4,4'-bis-hydroxyazobenzene and hexamethylenene diisocyanate. Hexamethylene diisocyanate played a connecting role in the polymer chain. The synthesis process is described in the Electronic Supplementary Material (ESM). The final product was a brown amorphous powder with chemical name poly (4,4'-bis-hydroxyazobenzene hexamethylene diisocyanate) (P-AZO-HDI).

2.2 Characterizations of P-AZO-HDI

The mass spectra of the P-AZO-HDI polymer were measured by gas chromatography mass spectrometry (GC/MS-QP2010). The P-AZO-HDI polymer was dissolved in acetone to obtain the tested samples. The IR absorption spectra were characterized by a Fourier transform infrared spectrometer (Bruker, Horiba, Germany). During the Infrared spectra measurements, the samples were prepared by the squash method to form a submillimeter thick film, and the test was

performed under atmospheric conditions at room temperature. The UV-visible absorption spectra were recorded on a UV-visible spectrophotometer (UV-2700, Shimadzu, Japan). The samples were composed of $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ P-AZO-HDI and N-methyl pyrrolidone (NMP) solution. The morphology of the powder or film formed of P-AZO-HDI was observed by scanning electron microscopy (SEM).

2.3 Photoisomerization experiments

To characterize the light-induced transition between the cis and trans isomers, P-AZO-HDI was illuminated by a mercury lamp (Philips, $\lambda = 210\text{--}380 \text{ nm}$). NIR irradiation was carried out by using an IR-250 RH lamp (Philips, $\lambda = 760\text{--}5,000 \text{ nm}$). Azobenzene can transform from the cis isomer into the trans isomer under the infrared thermal effect. Here, NIR light was used to achieve a rapid heating goal.

2.4 Viscosity measurements

The light-controlled viscosities of the photosensitive fluids were measured on an Anton Paar Physica (MCR302) rheometer. The test temperature was at an ambient temperature of 25°C . The cone-plate measuring system was selected to measure the viscosity. The diameter of the cone was 50 mm , and the cone-plate gap was equal to $103 \mu\text{m}$. The angle of the cone was 179° . The shear rates ranged from 1 to 300 s^{-1} , and the total test time was approximately 3 min for each sample. To explore the photoresponsive viscosity, each sample was adequately irradiated by UV/NIR light before testing. During the viscosity test, the samples and rheometer were sheltered to avoid the influence of ambient light.

2.5 Light-controlled friction measurements

The friction measurements of ceramic bearings with pure sliding system were conducted on a UMT3 tribometer. A Si_3N_4 ceramic bearing material was selected to achieve the light-controlled friction regulation. A ball-on-disk configuration was adopted to simulate the working conditions of the bearing. The sphere was a Si_3N_4 ball with a diameter of 10.7 mm , and the flat surface was a thin slice of SiO_2 . The test speeds ranged from 0 to $330 \text{ mm} \cdot \text{s}^{-1}$, and the speed

interval was $5.23 \text{ mm} \cdot \text{s}^{-1}$. The total test time was approximately 10 min , and the measurements were performed at room temperature (25°C). The load was set to 1 N , and a 500 g sensor was selected. As calculated by Hertzian elastic contact theory, the maximum Hertzian contact pressure was 289.1 MPa and the Hertzian contact radius was $40.6 \mu\text{m}$. The photosensitive fluid samples were the same as the viscosity-tested solutions, which included pure PEG200, PEG300, PEG400, and their corresponding solutions containing $2 \text{ wt\%}$ P-AZO-HDI. These samples were illuminated by NIR light or UV light for 2 min . After irradiation, the solutions were stored in a dark environment until the temperature recovered to 25°C .

2.6 Elastic modulus measurements

The Young's modulus of P-AZO-HDI flakes under UV/NIR light illumination was obtained by Atomic Force Microscope (AFM) *in situ* measurements under ambient conditions with shading treatment. The flakes of the P-AZO-HDI polymer were prepared by compression molding. First, 6 mg P-AZO-HDI powder was weighed and put into a square mold. Then, a 0.3 MPa pressure was maintained for 10 min on the mold. Finally, submillimeter transparent flakes were obtained by careful demolding. The flakes were fixed on a glass substrate, and the force curves were measured *in situ* under different irradiation conditions. In this work, a conical silicon probe was selected to survey the elastic modulus. The Young's modulus was obtained by fitting the force curves with the Hertz/Sneddon contact model. The fitting process can be found in the ESM.

2.7 Simulation calculation

The P-AZO-HDI property calculations were simulated by Material Studio 2017. The photoresponsive P-AZO-HDI polymer had two kinds of isomers, the trans isomer (NIR), and cis isomer (UV). There were three tasks, including chain morphology, shear modulus, and Young's modulus, for each isomer. The method to simulate the morphology was to optimize the geometric structure of the cis and trans isomers. Here, the end-to-end distance and radius of gyration of the P-AZO-HDI polymer were selected to characterize the morphology differences between the cis and trans isomers. Taking the degree of polymerization into

account, a series of polymers were simulated to observe the morphology of the cis/trans polymer. The shear modulus and Young's modulus were calculated by constructing an amorphous cell. The cell was formed with a certain proportion of polymers with different polymerization degrees. In this simulated calculation, the crystal building tool and Forcite tool were applied to optimize the geometry and calculate the mechanical properties. The detailed modeling and simulation process are listed in the ESM.

3 Results and discussions

3.1 Photoresponsive polymer P-AZO-HDI

The transformation between the cis isomer and trans isomer of azobenzene plays a decisive role in the light-controlled viscosity. The trans isomer can be converted to a cis isomer by irradiation with UV light, and recovers to the initial state when triggered by visible/light (NIR) stimuli, as shown in Fig. 1(a). The cis isomer and trans isomer of azobenzene have obvious differences in molecular length and structural conformation. To further magnify the differences in azobenzene properties, azobenzene was introduced into the main chain of the P-AZO-HDI polymer. The powder morphology of P-AZO-HDI was flowers in clusters, as

shown in Fig. 1(b). The UV-visible absorption spectrum of P-AZO-HDI was measured to determine the light-responsive wavelength, which was important for the design and application of light-controlled viscosity. There were two absorption peaks in the UV-visible spectrum of azobenzene. A strong peak was at 365 nm, and a weak peak was at 440 nm. In the UV-visible spectrum of the polymer, the 440 nm absorption peak was too weak to be submerged. The UV-visible spectrum of P-AZO-HDI with NMP as the solvent had a strong absorption peak at 365 nm in the primary state, as shown in Fig. 1(c). Then, after exposure to UV light for 2 min, the 365 nm absorption peak was quickly reduced. It was basically recovered to the initial value via illumination with NIR light for 2–5 min. In addition, the cis isomer can be converted to a trans isomer at temperatures higher than 80 °C. NIR light had an obvious advantage in its rapid heating to trigger the cis-trans transformation due to its excellent thermal effect. The results demonstrated that P-AZO-HDI had good photoresponsive properties triggered by NIR/UV light.

To analyze the functional groups of the P-AZO-HDI polymer, IR absorption spectroscopy was conducted, as shown in Fig. 1(d). The stretching vibration peaks of the N–H bonds (new bonds) and C–H₂ bonds were 3,331 and 2,933 cm^{−1}, respectively. The wavenumbers

Fig. 1 Basic characterization of the photosensitive polymer P-AZO-HDI. (a) Chemical structure of P-AZO-HDI and photoresponsive mechanism of azobenzene; (b) SEM image of the P-AZO-HDI powder; (c) UV-visible absorption spectra of the P-AZO-HDI polymer (The UV absorbed peak was at 365 nm); and (d) IR absorption spectrum of P-AZO-HDI (IR: 3,331 cm^{−1} (m; ν_s (NH)), 2,933 cm^{−1} & 2,856 cm^{−1} (m; ν_s (CH₂)), 1,617 cm^{−1} & 1,577 cm^{−1} (s; $\nu_{c=c}$ (Ar)), 645–950 cm^{−1} (m; ω (Ar–H))).

at 1,617 and 1,577 cm^{-1} were the vibration peaks of the benzene skeleton. The wavenumbers from 645 to 950 cm^{-1} were the stretching vibration peaks of the Ar–H bonds. The full IR spectral interpretation can be found in Fig. S1(a) in the ESM. P-AZO-HDI was the polycondensate of an azobenzene derivative and hexamethylene diisocyanate, as shown in Fig. 1(a) and Scheme S1 in the ESM. The C–H₂ bonds were from hexamethylene diisocyanate. The benzene skeleton and Ar–H bonds were from the azobenzene derivative. There were characteristic peaks of the two reactants in the IR spectrum of P-AZO-HDI. The results indicated that the polycondensation reaction was successfully ongoing. In addition, the mass spectrum (Fig. S1(b) in the ESM) was measured to determine the degree of polymerization of P-AZO-HDI. The degree of polymerization was spread across 7 to 20, and most polymers fell within 7 to 12. By roughly simulating the polymer structures, the molecular lengths of the P-AZO-HDI polymer were distributed from 10 to 40 nm. Therefore, the P-AZO-HDI was successfully synthesized through experimental and analytical results.

3.2 Light-controlled viscosity

The light-controlled viscosities of the P-AZO-HDI

and PEG200/300/400 solutions were measured on a cone-on-plate system. The tested shear rates ranged from 0 to 300 s^{-1} at 25 °C. The viscosities of four photorheological fluids (PEG300 and P-AZO-HDI) of different concentrations were tested to determine the best concentration. The variation rate (Δ) of the viscosity was defined as the increase in viscosity divided by the viscosity under NIR light. The variation rate of the viscosity increased as the P-AZO-HDI content increased, as shown in Fig. 2(a). The average variation rates were 5.1% for 0.5 wt% fluid, 7.5% for 1 wt% fluid, 10.7% for 1.5 wt% fluid, and 25.4% for 2 wt% fluid. The solubility of P-AZO-HDI in polyethylene glycol is close to 2 wt% at room temperature. The viscosities of 2 wt% P-AZO-HDI and PEG300 changed from 126.92 to 87.95 mPa·s under UV light as the shear rates increased from 0 to 300 s^{-1} . The viscosities of 2 wt% P-AZO-HDI and PEG300 ranged from 88.28 to 75.28 mPa·s when exposed to NIR light, as shown in Fig. 2(b). At most, there was a 43.8% rate of change. The dripping test of PEG300 and 2 wt% P-AZO-HDI solution under UV and NIR irradiation was recorded by camera. As shown in Fig. 2(c), after irradiation with UV or NIR light, 1 mL of the fluid was added to the pipettes. The dripping duration time of the NIR-irradiated liquid was 13.0 s, while the dripping

Fig. 2 Light-controlled viscosities of P-AZO-HDI and PEG300 solutions triggered by NIR/UV light. (a) Δ of photoresponsive PEG200 solutions with P-AZO-HDI concentrations of 0.5, 1.0, 1.5, and 2.0 wt%; (b) reversible light-controlled viscosity transformations of 2 wt% P-AZO-HDI and PEG300 solutions; and (c) photosensitive rheological fluid dripping test of 1 mL 2 wt% P-AZO-HDI and PEG300 solutions.

duration time of the UV-irradiated liquid was 19.5 s. This meant that the viscous forces of the fluids under UV light were higher than those under NIR light. Repeating the reversible light-controlled viscosity experiments several times, the viscosities of UV irradiation were typically higher than those of NIR light.

Most solutions of 2 wt% P-AZO-HDI mixed with polyethylene glycol (Figs. 2(b), 3(a), and 3(b)) behaved as non-Newtonian fluids with shear thinning properties. However, pure polyethylene glycol essentially maintained Newtonian fluid properties. The viscosities of solutions irradiated by UV light were typically higher than those irradiated by NIR light. At low shear rates, the viscosity difference was greater. When the shear rates were higher than 30 s^{-1} , the viscosity differences remained relatively stable. The viscosities of pure PEG200, pure PEG300, and pure PEG400 were 45.78 ± 2.057 , 66.97 ± 4.816 , and $93.35 \pm 0.385 \text{ mPa}\cdot\text{s}$, respectively. The viscosities of 2 wt% P-AZO-HDI and PEG200 exposed to UV light were 20–65 mPa·s higher than those irradiated by NIR light, as shown in Fig. 3(a). The change extent of the viscosities was up to 45.1%. The viscosities of the 2 wt% P-AZO-HDI and PEG400 solution irradiated by UV light were 10–17 mPa·s higher than those under NIR light, as shown in Fig. 3(b). The regulated rates ranged from 11.1% to 16.4%. In addition, the viscosities of the P-AZO-HDI and polyethylene glycol solutions were reversibly transformed by alternating UV and NIR light irradiation, as shown in Figs. 2(b) and S2(a), and S2(b) in the ESM. The results of the fatigue tests indicated that the light-controlled viscosities of P-AZO-HDI and polyethylene glycol had a stable and obvious regulation in the photosensitive rheological fluids.

Fig. 3 Light-controlled viscosities of 2 wt% P-AZO-HDI dissolved in (a) PEG200 solution and (b) PEG400 solution.

3.3 Mechanical properties of P-AZO-HDI

The mechanical and structural properties of the

P-AZO-HDI polymer played a significant role in the light-controlled viscosity regulation. The Young's modulus of P-AZO-HDI was determined by AFM *in situ* measurements. A diagram of the light-controlled Young's modulus measurement is shown in Fig. 4(a). The test sample was a thin film made by the squash method. There were two force curves obtained by extending and retracting the motions of the AFM probe. Here, the extending force curve was selected to fit as described in the ESM. A 160AC-NA standard silicon probe was adopted to measure force curves, as shown in Fig. S3(a) in the ESM. The fitting modulus was the Hertz/Sneddon elastic contact modulus, as shown in Fig. S3(b) in the ESM. The Young's modulus was 5.304 GPa when exposed to NIR light and 2.634 GPa when irradiated by UV light as shown in Fig. 4(b). The Young's modulus was repeated several times, and the average Young's modulus was $7.975 \pm 2.357 \text{ GPa}$ under NIR light and $3.039 \pm 0.351 \text{ GPa}$ under UV light, as shown in Fig. 4(c) and Table S2 in the ESM. The simulation results supported the Young's modulus measured by AFM. The Young's moduli of the simulation results were 0.526 GPa for the trans isomer (NIR) and 0.153 GPa for the cis isomer (UV), as shown in Fig. 4(d). There was a regular pattern in which the Young's modulus of the trans isomer (NIR) was significantly higher than that of the cis isomer (UV).

According to the simulated results of the polymer structures, there were obvious differences between the molecular morphologies of the trans isomer (NIR) and cis isomer (UV). The trans isomer polymers were mainly long linear-chain structures, while the cis isomer polymers were serrated-chain structures, as shown in Fig. S3(f) in the ESM. Here, the terminal distance and radius of gyration of the P-AZO-HDI polymers were selected to investigate the difference between the trans and cis polymers. The terminal distance of the polymer was defined by the length between the first atom and the last atom of the molecule. Molecules with longer terminal distance had better straightness at the same degree of polymerization. The terminal distances of the trans isomer (NIR) were generally 4.17–11.62 nm longer than that of the cis isomer (UV) as the degree of polymerization increased from 7 to 20, as shown in Fig. 4(e) and Table S1 in the ESM. There was a different of up to 33% in molecular length

Fig. 4 Mechanical performance and molecular simulation results of P-AZO-HDI. (a) Diagram of the light-controlled Young's modulus measurement by AFM; (b) fitting force curves of P-AZO-HDI (The Young's modulus was 5.304 GPa under NIR light and 2.634 GPa under UV light); (c) statistical chart of the reversible Young's modulus of the P-AZO-HDI film (The average Young's modulus was $7.975 \pm 2.357 \text{ GPa}$ under NIR light and $3.039 \pm 0.351 \text{ GPa}$ under UV light); (d) simulated results of mechanical properties (The Young's moduli were 0.526 GPa for the trans isomer (NIR) and 0.153 GPa for the cis isomer (UV). The shear moduli were 0.534 GPa for the trans isomer and 0.339 GPa for the cis isomer); and (e) results of the molecular conformation simulation (Light-controlled molecular structures with a series of degrees of polymerization were characterized by terminal distance and radius of gyration).

between the trans and cis polymers at the same degree of polymerization. In general, a smaller radius of gyration represented a more twisted polymer. The radius of gyration of the trans isomer (NIR) was up to 24% larger than that of the cis isomer (UV). The simulated results indicated that the trans isomer was straighter than the cis isomer. In addition, the simulated shear modulus of the trans isomer polymer was 0.534 GPa while that of the cis isomer polymer was 0.339 GPa, as shown in Fig. 4(e). The mechanical properties and molecular structure differences between the trans and cis isomers provided the possibility of achieving light-controlled viscosity.

3.4 Friction regulation by photosensitive rheological fluids

According to the Hamrock–Dowson film thickness formula (Eqs. (S5) and (S6) in the ESM), the film thickness of the contacted areas will increase 0.67% as the viscosity increases 1%. Therefore, the light-controlled viscosity of rheological fluids had an important influence on the friction of contact area, especially in the boundary lubrication and mixed lubrication. The photosensitive rheological fluid is

potential to application in the light-induced intelligent braking of some devices, such as dampers, gears, and bearings. Here, the friction measurement of ceramic sliding bearings (Fig. 5(a)) was conducted on a universal mechanical tester type 3 (UMT3) adopting a point contact mode. The silicon nitride sliding bearing and the diagram of light-controlled friction are shown in Fig. 5(b). The COF of pure PEG200/300/400 was also measured, as shown in Fig. 5(c). The COF of pure PEG200/300/400 first decreased and then remained relatively stable as the test speeds increased from 0 to $330 \text{ mm}\cdot\text{s}^{-1}$. The coefficients of friction (COFs) that changed with test speeds from 0 to $330 \text{ mm}\cdot\text{s}^{-1}$ were recorded under NIR/UV light. The COF of the 2 wt% P-AZO-HDI and polyethylene glycol solutions had obvious differences after irradiation by NIR/UV light, especially when the test speeds were lower than $180 \text{ mm}\cdot\text{s}^{-1}$, as shown in Fig. 5(d). However, the light-controlled friction lost effectiveness at speeds greater than $180 \text{ mm}\cdot\text{s}^{-1}$. It was conjectured that the lubricated state had been transformed from mixed lubrication to elastohydrodynamic lubrication at a speed of $180 \text{ mm}\cdot\text{s}^{-1}$. Because the thickness of lubricated film was about 15 nm at the speed of $150 \text{ mm}\cdot\text{s}^{-1}$ and

the comprehensive surface roughness was 5 nm. In elastohydrodynamic lubrication, the film thickness separates the contacted interface by a thick fluid layer. Therefore, the COFs under UV and NIR light were almost the same at speeds greater than 180 mm·s⁻¹. The COFs under NIR light were much higher than those under UV light at speeds below 180 mm·s⁻¹, as shown in Figs. 5(e)–5(g). Whether under UV or NIR light irradiation, the COF change trend of P-AZO-HDI in different polyethylene glycols followed similar rules, decreasing first and then increasing slowly as the speed increased.

Here, the COF ratio was defined by the COF under NIR light divided by that under UV light at the same speed. The COF ratio was selected to measure

the regulating performances of the photosensitive rheological fluids. The maximum COF ratios were 3.77 in PEG200 and 2 wt% P-AZO-HDI solution at the speed of 68 mm·s⁻¹, 2.35 in PEG300 and 2 wt% P-AZO-HDI solution at the speed of 26 mm·s⁻¹, and 2.85 in PEG400 and 2 wt% P-AZO-HDI solution at the speed of 10 mm·s⁻¹, as shown in Fig. 5(d). The COF change ranges were 20%–100% in other works of light-induced friction [5, 55, 56]. Further studies of light-controlled friction fatigue tests showed that the friction regulations underwent reversible transformation under UV and NIR light, as shown in Fig. 5(h). The COF of PEG200 and 2 wt% P-AZO-HDI tended to alternate between 0.056 ± 0.0098 (NIR) and 0.015 ± 0.0066 (UV) at the speed of 68 mm·s⁻¹. The COF of PEG300

Fig. 5 Regulation of the COF for ceramic bearings by photosensitive rheological fluids. (a) Pictures of the ceramic sliding bearings and friction tests on UMT tribometers; (b) diagram of friction measurements regulated by UV/NIR light; (c) COF of pure PEG 200/300/400 solutions for varying test speeds; (d) COF ratio was defined by the COF under NIR light divided by that under UV light (The largest regulated ratios of the photosensitive rheological fluids were 3.77 in PEG200, 2.35 in PEG300, and 2.85 in PEG400); (e) COF of 2 wt% P-AZO-HDI and PEG200 solutions for test speeds from 0 to 330 mm·s⁻¹; (f) COF of 2 wt% P-AZO-HDI and PEG300 solution for varying test speeds; (g) COF of 2 wt% P-AZO-HDI and PEG400 solution for varying test speeds; and (h) reversible friction regulation achieved by P-AZO-HDI and polyethylene glycol solutions (The COF tended to alternately change between 0.056 ± 0.0098 (NIR) and 0.015 ± 0.0066 (UV) at the speed of 68 mm·s⁻¹ in PEG200 and 2 wt% P-AZO-HDI solution, between 0.055 ± 0.0076 (NIR) and 0.023 ± 0.0055 (UV) at the speed of 26 mm·s⁻¹ in PEG300 and 2 wt% P-AZO-HDI, and between 0.083 ± 0.0084 (NIR) and 0.029 ± 0.0010 (UV) at the speed of 10 mm·s⁻¹ in PEG400 and 2 wt% P-AZO-HDI).

and 2 wt% P-AZO-HDI changed from 0.055 ± 0.0076 irradiated by NIR light to 0.023 ± 0.0055 when exposed to UV light at the speed of $26 \text{ mm} \cdot \text{s}^{-1}$. The COF of PEG400 and 2 wt% P-AZO-HDI varied from 0.083 ± 0.0084 (NIR) to 0.029 ± 0.0010 (UV) at a speed of $10 \text{ mm} \cdot \text{s}^{-1}$. The results indicated that the photosensitive rheological fluids effectively regulated the friction of ceramic sliding bearings.

3.5 Regulating mechanisms of light-controlled viscosity and friction

According to the results of the simulations and experiments, the molecular structure differences before and after UV irradiation played a decisive role in the light-controlled viscosity. The trans isomer molecules under NIR light were long linear-chain structures,

whereas the cis isomer molecules under UV light had serrated-chain morphologies, as shown in Fig. S3(f) in the ESM. The molecular length of the trans isomer was up to 33% longer than that of the cis isomer. The cone-plate viscosity measurement system was simplified as shown in Fig. 6(a). The higher viscosity was due to the greater possibility of twining on the vertical shear plane. Because the cis isomer of P-AZO-HDI had a serrated-chain morphology, a higher shear force is needed to overcome the resistance of the molecular tangle. In contrast, the trans isomer of P-AZO-HDI had a linear-chain structure and shear occurred easily due to almost no entanglement between these straight chains. This meant that the viscosity under NIR light was much smaller than that under UV light.

There were two critical factors, the photosensitivity of the rheological fluids and the mechanical properties

Fig. 6 Mechanisms of light-controlled viscosity and friction. (a) Light-controlled viscosity was ascribed to the structural differences between the trans and cis isomers of P-AZO-HDI (The P-AZO-HDI cis isomer was a serrated-chain structure, which meant that it was more likely to twine during shearing. The lower viscosity under NIR light was due to the linear-chain structure of the trans isomer) and (b) two factors (photosensitive fluids and mechanical properties of the P-AZO-HDI layer in contact areas) accounted for light-controlled friction (The higher viscosities (UV) meant thicker lubricated film. Therefore, frictional pairs were more likely to separate under UV light, which led to a lower COF. In addition, the P-AZO-HDI layer easily sheared and deformed, leading to a lower COF under UV light due to the smaller shear modulus and Young's modulus. In contrast, the higher COF under NIR light was due to the anti-shear and anti-deformation properties of the P-AZO-HDI layer with a larger shear modulus and Young's modulus. The photosensitive fluids and mechanical properties of the P-AZO-HDI layer worked together to regulate friction).

of the P-AZO-HDI layer, which accounted for the friction regulation of ceramic sliding bearings. The mechanism of friction regulation (Fig. 6(b)) was divided into two parts. The first factor was the lubricated film thickness difference induced by the photosensitive fluid. In the boundary lubrication and the mixed lubrication (low speeds), the thickness of lubricated film has a significant influence on friction coefficient. According to Eq. (S6) in the ESM, the film thickness of 2 wt% P-AZO-HDI and PEG200 (Fig. 6(b)) under UV light was up to 30.2% thicker than that under NIR light. The lubrication film thickness ranges (Figs. S4(a) and S4(b) in the ESM) were up to 29.3% greater in the 2 wt% P-AZO-HDI and PEG300 solutions and up to 11.0% greater in the 2 wt% P-AZO-HDI and PEG400 solutions. The results indicated that the frictional pairs were more likely to be separated by a thicker film layer, leading to a smaller COF under UV light. The two surfaces were more likely to come into contact under NIR light, contributing to higher friction. When the speeds were higher than $180 \text{ mm}\cdot\text{s}^{-1}$, the lubricated state was elastohydrodynamic lubrication. The friction pair was separated by elastohydrodynamic fluid film, which led to the close friction coefficients under UV and NIR light.

The second factor was the mechanical property difference of the P-AZO-HDI layer on the contact areas. Here, the mechanical properties included the shear moduli and Young's moduli of the trans and cis isomers. As the results of the mechanical properties of P-AZO-HDI showed, the Young's modulus under NIR light was 2.62 times that of the modulus under UV light, as measured by AFM. The regulated range of the Young's modulus was 3.44 times according to the simulation of the mechanical properties. In addition, the simulated shear modulus under NIR light was 1.58 times that of the modulus under UV light. It was speculated that the P-AZO-HDI layer was hard to shear and deform with shearing direction due to the larger Young's modulus and shear modulus under NIR light. Therefore, the anti-shear and anti-deformation properties led to a higher COF under NIR light. When exposed to UV light, the P-AZO-HDI layer easily sheared and deformed with the shearing direction owing to the smaller Young's modulus and shear modulus. The bedding-shear and easy-to-deform

P-AZO-HDI layers resulted in smaller COFs under UV light. In conclusion, the photosensitive rheological fluids and mechanical properties of the P-AZO-HDI layer worked together to achieve light-controlled friction of ceramic sliding bearings.

4 Conclusions

In summary, we designed a group of photosensitive rheological fluids composed of 2 wt% poly (4,4'-bis-hydroxyazobenzene hexamethylene diisocyanate) (P-AZO-HDI) and polyethylene glycol. These fluids can achieve reversible viscosity regulation via the obvious differences in the structural and mechanical properties under UV compared to NIR light. The P-AZO-HDI polymer with azobenzene units as the backbone was designed as a photoresponsive functional material. The molecular length under NIR light was 33% longer than that under UV light. The mechanical properties, such as the shear modulus and Young's modulus, were also significantly different under UV/NIR light. The regulated ranges of light-controlled viscosity were increased by 45.1% in PEG200, 43.8% in PEG300, and 16.4% in PEG400. Photosensitive rheological fluids were used to achieve reversible friction regulation of ceramic sliding bearings. The maximum COF regulated ranges were 3.77 times greater in PEG200, 2.35 times greater in PEG300, and 2.85 times greater in PEG400. The mechanism of the light-controlled viscosity was ascribed to the structural differences between the trans and cis isomers of P-AZO-HDI. The friction regulation of ceramic bearings was due to the photosensitive fluids and mechanical properties of the P-AZO-HDI layer. The light-controlled viscosity, light-controlled shear modulus, and light-controlled Young's modulus worked together to regulate friction. This work not only provides a strategy to design photoresponsive polymers with quite different structures under UV/NIR irradiation but also develops new intelligent rheological fluids based on light stimuli. These results are significant for understanding the mechanism of viscosity and friction regulation from scientific and technological views. Photosensitive fluids have wide applications in smart rheological fluids, liquid transport, intelligent lubrication, and photoforce sensors.

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References

- [1] Liu Y, Tan L. Method of C groove on vortex suppression and energy performance improvement for a NACA0009 hydrofoil with tip clearance in tidal energy. *Energy* **155**: 448–461 (2018)
- [2] Cheng H Y, Bai X R, Long X P, Ji B, Peng X X, Farhat M. Large eddy simulation of the tip-leakage cavitating flow with an insight on how cavitation influences vorticity and turbulence. *Appl Math Model* **77**: 788–809 (2020)
- [3] Lv J A, Liu Y Y, Wei J, Chen E Q, Qin L, Yu Y L. Photocontrol of fluid slugs in liquid crystal polymer microactuators. *Nature* **537**(7619): 179 (2016)
- [4] Ma L, Gaisinskaya-Kipnis A, Kampf N, Klein J. Origins of hydration lubrication. *Nat Commun* **6**(1): 6060 (2015)
- [5] Tang S, Xue D, Guo J, Ma L, Tian Y, Luo J. Macroscale Light-Controlled Lubrication Enabled by Introducing Diarylethene Molecules in a Nanoconfinement. *Langmuir* **36**(21): 5820–5828 (2020)
- [6] Martín-Alfonso J E, Martín-Alfonso M J, Valencia C, Cuberes M T. Rheological and tribological approaches as a tool for the development of sustainable lubricating greases based on nano-montmorillonite and castor oil. *Friction* **9**(2): 415–428 (2021)
- [7] Gao M, Li H, Ma L, Gao Y, Ma L, Luo J. Molecular behaviors in thin film lubrication—Part two: Direct observation of the molecular orientation near the solid surface. *Friction* **7**(5): 479–488 (2019)
- [8] Ma L, Luo J. Thin film lubrication in the past 20 years. *Friction* **4**(4): 280–302 (2016)
- [9] Jin Y, Chen F, Xu J, Yuan X. Nonlinear dynamic analysis of low viscosity fluid-lubricated tilting-pad journal bearing for different design parameters. *Friction* **8**(5): 930–944 (2020)
- [10] Jin Y, Shi Z, Zhang X, Yuan X. Rapid solution for analysis of nonlinear fluid film force and dynamic behavior of a tilting-pad journal bearing-rotor system with turbulent and thermal effects. *Friction* **8**(2): 343–359 (2020)
- [11] Wu Z. Multi-scale simulation of three-dimensional thin-film lubrication. *Friction* **9**(3): 471–487 (2021)
- [12] Liu J, Zang C, Tian S, Liu J, Yang H, Jia S, You L, Liu B, Zhang M. Water conservancy projects in China: Achievements, challenges and way forward. *Glob Environ Change* **23**(3): 633–643 (2013)
- [13] Li X, Dao M, Lykotrafitis G, Karniadakis G E. Biomechanics and biorheology of red blood cells in sickle cell anemia. *J Biomech* **50**: 34–41 (2017)
- [14] Ji X, Zhang W, Jia W, Wang X, Tian Y, Deng L, Liu J. Cactus-like double-shell structured SiO₂@TiO₂ microspheres: Fabrication, electrorheological performances and microwave absorption. *J Ind Eng Chem* **56**: 203–211 (2017)
- [15] Liu C, Meng Y, Jia W, Zhang W, Zhao Q, Tian Y. Peanut shaped titanium oxide micro-particles achieved by cathode plasma electrolysis and their electrorheological characteristics. *Smart Mater Struct* **27**(11): 115017 (2018)
- [16] Yun G, Tang S-Y, Sun S, Yuan D, Zhao Q, Deng L, Yan S, Du H, Dickey M D, Li W. Liquid metal-filled magnetorheological elastomer with positive piezoelectricity. *Nat Commun* **10**(1): 1300 (2019)
- [17] Chen K, Shan L, Zhang X, Meng Y. Squeeze behaviors of magnetic powders between two parallel plates. *Smart Mater Struct* **23**: 117004 (2014)
- [18] Paul P S, Iasanth J A, Vasanth X A, Varadarajan A S. Effect of nanoparticles on the performance of magnetorheological fluid damper during hard turning process. *Friction* **3**(4): 333–343 (2015)
- [19] Li R, Li X, Li Y, Yang P-A, Liu J. Experimental and numerical study on surface roughness of magnetorheological elastomer for controllable friction. *Friction* **8**(5): 917–929 (2020)

- [20] Lian C, Lee K-H, An J-W, Lee C-H. Effect of stick–slip on magneto-rheological elastomer with a magnetic field. *Friction* **5**(4): 383–391 (2017)
- [21] Chu Z L, Feng Y J. pH-switchable wormlike micelles. *Chem Commun* **46**(47): 9028–9030 (2010)
- [22] Lee H-Y, Diehn K K, Sun K, Chen T, Raghavan S R. Reversible photorheological fluids based on spiropyran-doped reverse micelles. *J Am Chem Soc* **133**(22): 8461–8463 (2011)
- [23] Yang D, Zhao J. A light-responsive organofluid based on reverse worm-like micelles formed from an equi-charged, mixed, anionic gemini surfactant with an azobenzene spacer and a cationic conventional surfactant. *Soft Matter* **12**(17): 4044–4051 (2016)
- [24] Chu Z, Dreiss C A, Feng Y. Smart wormlike micelles. *Chem Soc Rev* **42**(17): 7174 (2013)
- [25] Sparrow E M, Abraham J P, Gorman J M. *Advances in Heat Transfer*. San Diego(USA): Elsevier, 2018.
- [26] Zhang X-D, Liu J. Perspective on liquid metal enabled space science and technology. *Sci China Technol Sc* **63**(7): 1127–1140 (2020)
- [27] Chen C, Liao W-H. A self-sensing magnetorheological damper with power generation. *Smart Mater Struct* **21**(2): 025014 (2012)
- [28] Aguirre N, Ikhouane F, Rodellar J, Christenson R. Parametric identification of the Dahl model for large scale MR dampers. *Struct Control Health Monit* **19**(3): 332–347 (2012)
- [29] Abramov V O, Abramova A V, Bayazitov V M, Mullakaev M S, Marnosov A V, Ildiyakov A V. Acoustic and sonochemical methods for altering the viscosity of oil during recovery and pipeline transportation. *Ultrason Sonochem* **35**: 389–396 (2017)
- [30] Abbadie A, Crescente F, SèMèRia M N. Advanced wet cleanings post-CMP. *J Electrochem Soc* **151**(1): G57 (2004)
- [31] Akagami Y, Asari K, Jeyadevan B, Fujita T. Characterization of particle motion for polishing and texturing under AC field by using Ppricle dispersion type ER fluid. *J Intel Mat Syst Str* **9**(8): 672–675 (1998)
- [32] Liu C, Meng Y, Tian Y. Potential-controlled boundary lubrication using MoS₂ additives in diethyl succinate. *Tribol Lett* **68**(3): 72 (2020)
- [33] Amann T, Gatti F, Oberle N, Kailer A, Rùhe J. Galvanically induced potentials to enable minimal tribochemical wear of stainless steel lubricated with sodium chloride and ionic liquid aqueous solution. *Friction* **6**(2): 230–242 (2018)
- [34] Zhang S, Qiao Y, Liu Y, Ma L, Luo J. Molecular behaviors in thin film lubrication—Part one: Film formation for different polarities of molecules. *Friction* **7**(4): 372–387 (2019)
- [35] Meng Y, Xu J, Jin Z, Prakash B, Hu Y. A review of recent advances in tribology. *Friction* **8**(2): 221–300 (2020)
- [36] Su J, Teng J, Xu Z, Li Y. Corrosion-wear behavior of a biocompatible magnesium matrix composite in simulated body fluid. *Friction*, **10**(1): 31–43 (2022)
- [37] Sun X, Guo R, Yuan B, Chen S, Wang H, Dou M, Liu J, He Z-Z. Low-temperature triggered shape transformation of liquid metal microdroplets. *ACS Appl Mater Interfaces* **12**(34): 38386–38396 (2020)
- [38] Groten J, Bunte C, Ruhe J. Light-induced switching of surfaces at wetting transitions through photoisomerization of polymer monolayers. *Langmuir* **28**(42): 15038–15046 (2012)
- [39] Han B, Zhang Y-L, Chen Q-D, Sun H-B. Carbon-based photothermal actuators. *Adv Funct Mater* **28**(40): 1802235 (2018)
- [40] Ichimura K, Oh S K, Nakagawa M. Light-driven motion of liquids on a photoresponsive surface. *Science* **288**(5471): 1624–1626 (2000)
- [41] Uyama A, Yamazoe S, Shigematsu S, Morimoto M, Yokojima S, Mayama H, Kojima Y, Nakamura S, Uchida K. Reversible photocontrol of surface wettability between hydrophilic and superhydrophobic surfaces on an asymmetric diarylethene solid surface. *Langmuir* **27**(10): 6395–6400 (2011)
- [42] Charati M B, Lee I, Hribar K C, Burdick J A. Light-sensitive polypeptide hydrogel and nanorod composites. *Small* **6**(15): 1608–1611 (2010)
- [43] Wani O M, Zeng H, Priimagi A. A light-driven artificial flytrap. *Nat Commun* **8**:15546 (2017)
- [44] Deng J, Li J, Chen P, Fang X, Sun X, Jiang Y, Weng W, Wang B, Peng H. Tunable photothermal actuators based on a pre-programmed aligned nanostructure. *J Am Chem Soc* **138**(1): 225–230 (2016)
- [45] Pardo R, Zayat M, Levy D. Photochromic organic–inorganic hybrid materials. *Chem Soc Rev* **40**(2): 672 (2011)
- [46] Andréasson J, Pischel U. Molecules with a sense of logic: A progress report. *Chem Soc Rev* **44**(5): 1053–1069 (2015)
- [47] Li H, Wang J. Ultrafast yet controllable dual-responsive all-carbon actuators for implementing unusual mechanical movements. *ACS Appl Mater Interfaces* **11**(10): 10218–10225 (2019)
- [48] Wang S, Gao Y, Wei A, Xiao P, Liang Y, Lu W, Chen C, Zhang C, Yang G, Yao H, Chen T. Asymmetric elastoplasticity of stacked graphene assembly actualizes programmable untethered soft robotics. *Nat Commun* **11**(1): 4359 (2020)
- [49] Lee C K, Beiermann B A, Silberstein M N, Wang J, Moore J S, Sottos N R, Braun P V. Exploiting force sensitive spiropyran as molecular level probes. *Macromolecules* **46**(10): 3746–3752 (2013)
- [50] Gao J, He Y, Xu H, Song B, Zhang X, Wang Z, Wang X. Azobenzene-containing supramolecular polymer films for laser-induced surface relief gratings. *Chem Mater* **19**(1): 14–17 (2007)

- [51] Kumar G S, Neckers D C. Photochemistry of azobenzene-containing polymers. *Chem Rev* **89**(8): 1915–1925 (1989)
- [52] Renth F, Siewertsen R, Temps F. Enhanced photoswitching and ultrafast dynamics in structurally modified photochromic fulgides. *Int Rev Phys Chem* **32**(1): 1–38 (2013)
- [53] Beharry A A, Woolley G A. Azobenzene photoswitches for biomolecules. *Chem Soc Rev* **40**(8): 4422–4437 (2011)
- [54] Ihalainen J A, Bredenbeck J, Pfister R, Helbing J, Chi L, van Stokkum I H M, Woolley G A, Hamm P. Folding and unfolding of a photoswitchable peptide from picoseconds to microseconds. *P Natl Acad Sci USA* **104**(13): 5383 (2007)
- [55] Nanni G, Ceseracciu L, Oropesa-Nunez R, Canale C, Salvatore P, Fragouli D, Athanassiou A. Tunable friction behavior of photochromic fibrillar surfaces. *Langmuir* **31**(22): 6072–6077 (2015)
- [56] Liu D, Broer D J. Light controlled friction at a liquid crystal polymer coating with switchable patterning. *Soft Matter* **10**(40): 7952–7958 (2014)

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