Technical Note

Chemically-adhesive particles form stronger and stiffer magnetorheological fluids

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Abstract
Magnetorheological fluids (MRFs) are suspensions of magnetic particles that solidify in the presence of a magnetic field due to the particles forming chains along field lines. The magnetic forces between particles dominate the solidification process and determine the yield stress of the resulting solid. Here, we investigate how reversible chemical links between particles influence MRF behavior in terms of their yield stress and stiffness through rheological testing in flow and oscillation mode. Initially, we functionalize particles with phosphonate groups that are expected to link through hydrogen bonding and find that this MRF exhibits up to 40% higher yield stress and 100% higher stiffness than an MRF composed of unfunctionalized particles. To explain this change, we model the chemical attraction as an adhesion that supplements dipole–dipole interactions between particles. Interestingly, we find that the increase in yield stress is largest for dilute suspensions that are expected to solidify into isolated chains, while the proportional increase in yield stress is less for MRF with higher concentrations. This is explained by the higher concentration MRF forming a body-centered tetragonal lattice in which interparticle adhesion forces are no longer aligned with the applied field. To explore the possibility of dynamically tuning interparticle interactions, we functionalize particles with polystyrene polymers with thymine terminal groups that will only exhibit interparticle hydrogen bonding in the presence of a small linking molecule, namely melamine. We find that MRF formed with these particles also exhibit up to a 40% increase in yield stress and ~100% increase in stiffness for the polymer grafted particles in the presence of melamine, due to the formation of hydrogen bonding linkages between the thymine and melamine groups. In addition to confirming the role of hydrogen bonding in increasing MRF stiffness and yield stress, these results highlight the possibility of dynamically tuning MRF performance using magnetic fields and chemical modifications.

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(Some figures may appear in color only in the online journal)
2. Methods

2.1. Synthesis of magnetorheological fluids

2.1.1. Phosphonate-functionalized MRF. To synthesize MRF with chemically-adhesive particles, a method was adapted from Othmani et al. [20] to functionalize carbonyl iron microparticles (3–5 μm size, Skyspring Nanomaterials, 0990JH), shown in figure 1(c), with phosphonate groups that are predicted to adhere particles to one another through hydrogen bonding when they are in close contact, as depicted in figure 1(d). Specifically, a 1 mM etidronic acid solution was made by adding 17.2 μL of etidronic acid (60% aqueous solution, Sigma Aldrich, H6773) to 50 mL deionized (DI) water which was neutralized to pH 7 using 10 mg sodium hydroxide (Sigma Aldrich, S8045). Then, 0.5 g of carbonyl iron was added and the vial was rotated on a mechanical spinner for 48 h. After spinning, the particles were washed five times with DI water and then dried overnight.

Functionalized particles were then added to a 10 mM NaCl aqueous solution (Sigma Aldrich, S7653) at 2, 4, 8, and 14.2 vol% to make the pMRF. NaCl was included to screen any electrostatic repulsion that might arise from added charge from the etidronic acid on the particle surface.

2.1.2. Conventional MRF. To facilitate comparison with the pMRF, the particles for the cMRF were treated according to the same steps as above except without etidronic acid or sodium hydroxide being added to the solution prior to mixing in the mechanical stirrer. The iron particles were washed and dried in the same way and also added to the 10 mM NaCl solution at 2, 4, 8, or 14.2 vol%.

2.1.3. Thymine-functionalized MRF. To prepare the thymine-functionalized particles, we started by synthesizing a thymine-terminated polystyrene polymer with a phosphonate anchor group according to the procedure reported previously by Santos and Macfarlane [21]. In brief, we first synthesized the thymine-functionalized atom transfer radical polymerization (ATRP) initiator and the propargyl phosphate cyclohexamine salt. The thymine ATRP initiator was then used to synthesize a 10 kDa polystyrene polymer via ATRP. Following which, the alkyn functionalized phosphonate was added to the polymer via copper(I) catalyzed azide alkyn cycloadDITION to yield the final thymine-functionalized polymer.

To graft the thymine-functionalized polymers onto the carbonyl iron particles, we first activated the surface of the particles by treating them with 0.5 M hydrochloric acid [22]: 2.0 g of particles were added to 30 mL of 0.5 M hydrochloric acid and then mechanically shaken for 40 min. The treated particles were washed eight times with DI water and then dried overnight under vacuum. To make each batch of thymine-functionalized particles, 250 mg of activated particles, 39 mg of thymine-functionalized polymer, and 1.5 mL of toluene were added to a 1.5 mL Eppendorf tube. The mixture was sonicated briefly to ensure that the polymers were fully dissolved in toluene before being mechanically shaken at 700 RPM at 70 °C for 15 h. The thymine-functionalized particles were then washed six times with toluene and dried overnight under high vacuum. Finally, the functionalized particles were added to anisole at ϕ = 2, 4, and 8 vol% to make the thymine-functionalized MRF (tMRF).

2.1.4. Thymine-functionalized MRF with melamine. In order to link the thymine-functionalized particles, melamine was used as a small linking molecule. First, a 99 mM melamine solution was made by mixing 25 mg of melamine (Sigma Aldrich, M2659) with 1 mL dimethylsulfoxide (Sigma Aldrich, D8418) and sonicating the solution for 10 min to fully dissolve the melamine. Then 1 mL of dimethylformamide (Sigma Aldrich, 72438) was added to the solution and vortexed until mixed. Directly before an experiment, 5 μL of the melamine solution was added to 995 μL of anisole (Sigma Aldrich, 123226) to form a 495 μM solution of melamine. Then, particles were added to the 495 μM melamine solution for ϕ = 2, 4, and 8 vol% samples and immediately used in the rheometer where the field was applied in order to promote adhesion between assembled particles through hydrogen bonding, thus making tMRF + mel.

2.2. Rheology

All samples were sonicated for 2 min prior to rheological testing to break up any particle aggregates that resulted from the drying process. Then, 85 μL samples were immediately pipetted onto the rheometer (TA Instruments, DHR-1 with Magnetorheology Accessory) with a plate–plate geometry for testing and the rheometer gap height was set to 250 μm for all experiments. Prior to shearing the MRF, B was applied to allow the particles to adhere when aligned. Specifically, magnetic field B was applied in steps of 0.1 T from B = 0.1 to 0.8 T with 1 min between each step. Then, flow-mode rheology was conducted by varying the shearing strain rate γ logarithmically spaced from 0.8 T decreasing down to 0.03 T. Samples were demagnetized between each B to reduce the effects of residual magnetization. Each trial was repeated three times with a fresh sample.

Oscillation-mode rheology was conducted by loading the sample in the same manner as used in flow mode and then B was increased from 0.1 to 0.5 T in steps of 0.1 T, similar to the flow-mode measurements, to allow for adhesion of the particles prior to testing. Then, measurements were conducted at B = 0.5 T by setting a range of τ that encompassed the solid and liquid-like regions of the MRF at B = 0.5 T. This range varied for the different ϕ tested. As τ was increased, the storage modulus G′ and loss modulus G″ were measured. Finally, each sample condition was repeated with a fresh sample for a total of three trials.

3. Results and discussion

In order to determine the influence of adhesive particles on MRF performance, pMRF and cMRF were compared using
flow-mode rheology. The measured $\tau$ exhibited by each fluid increased with $\varphi$, as shown in figure 2(a) for cMRF, and also increased dramatically with $B$. To quantify $\tau_0$, $\tau$ was measured vs $\dot{\gamma}$ as shown in figure 2(b) for both the cMRF and pMRF. This data was fit to the Bingham plastic constitutive model which is frequently used to model MRF behavior [2, 23–25],

$$\tau = \eta_B \dot{\gamma} + \tau_0,$$

where $\tau_0$ is the y-intercept of the curve and $\eta_B$ is the Bingham viscosity. While the Bingham plastic model is the most common method used to determine $\tau_0$ for MRF [9, 24, 26], it has been shown that there are more accurate methods to quantify $\tau_0$, such as using controlled-stress measurements or more complicated constitutive models [24, 27] which could be used to refine the $\tau_0$ measurement. That said, quantifying performance using the Bingham plastic $\tau_0$ is important because it provides a common benchmark among the MRF community. By repeating the measurements in figure 2(b) for logarithmically spaced $B$ between 0.03 and 0.8 T, $\tau_0$ was plotted vs $B$ to compare both fluids. As shown in figure 2(c) for $\varphi = 2$ vol%, pMRF exhibited a higher $\tau_0$ than cMRF for all $B$ tested. For each condition, three trials were conducted and averaged. After repeating this process for all $\varphi$, the percent increase in $\tau_0$ due to the adhesive functionalization was calculated and plotted in figure 2(d). These data clearly show that the adhesive functionalized particles increased $\tau_0$ by up to 40%, but in a $\varphi$-dependent manner with sparse particle suspensions exhibiting greater strengthening. While the nature of the $\varphi$-dependence was not yet clear, the increase in $\tau_0$ validated the hypothesis that additional adhesive force strengthened the solidified MRF.

Due to the added adhesive force for assembled particles, we hypothesized that the solidified pMRF would exhibit higher stiffness than the cMRF, which is another important performance metric for MRF applications [28–30]. In order to quantify the stiffness of the assembled particles, oscillation-mode rheology was used. In oscillation mode, shown in figure 3(a), the rheometer top plate oscillated back and forth in a $\tau$-controlled measurement where $\tau$ was applied and the strain $\gamma$ of the assembled particles was measured so that $G'$ and $G''$ of the material could be quantified. A representative plot of $G'$ and $G''$ for the cMRF is shown in figure 3(b). While high $\tau$ behavior can be used to determine the onset of shear melting, the
stiffness of the material is defined as the plateau \( G' \) at low \( \tau \). To compare the stiffness for the two fluids, \( G' \) vs \( \tau \) was measured for pMRF and cMRF at both \( \varphi = 2 \) and 8 vol\%. In figure 3(c), pMRF was observed to exhibit higher \( G' \) than the cMRF. The stiffness was quantified by fitting the plot of \( G' \) in log–log space to a power law with a \( y \)-offset which represented the extrapolated plateau \( G_0 \),

\[
\log(G') = a \times \log(\tau)^n + G_0
\]  

(2)

where \( a \) and \( n \) were additional fitting parameters. Interestingly, the pMRF plateau stiffness \( G_{0, p} \) was about twice as large as the cMRF plateau stiffness \( G_{0, c} \) for both \( \varphi \), as shown by their ratios in figure 3(d).

While the flow and oscillation-mode testing revealed that adhesive functionalization strengthened and stiffened the MRF, the strengthening was strongly \( \varphi \) dependent with the difference in \( \tau_0 \) decreasing as \( \varphi \) increased. In order to understand this dependence, we considered how the structure of the solidified MRF changes as \( \varphi \) increases. For low \( \varphi \), the MRF is understood to solidify as a series of isolated particle chains as depicted in figure 4(a) with a height determined by the rheometer gap. As a result, the magnetic dipoles that align with \( B \) were also in alignment with \( F_A \), so that both magnetic and adhesive contributions were acting in the same direction. However, at higher \( \varphi \), MRF solidify into columns of BCT solids as shown in figure 4(b) due to interactions between neighboring chains causing isolated chains to combine [31–33]. Interestingly, MRF chains have been observed to interact and start forming columnar structures in both simulation and experiment at \( \varphi > 5 \) vol\% [34, 35] which indicates that the transition from isolated chains to BCT columns is expected in the range of \( \varphi \) tested here. In such a BCT structure, the interparticle contacts would no longer be in the direction of the applied field, meaning that \( F_A \) was also no longer aligned with the magnetic force. Therefore, as the chains were sheared, \( F_A \) between particles broke at lower \( \gamma \) than \( F_M \) and contributed less to the strength of the assembled particles during failure. This likely explained why the strengthening associated with chemical adhesion decreased as \( \varphi \) increased, whereas the increase in \( G_0 \) was similar between the two structures due to the stiffness being measured at very low \( \gamma \) when the chains or columns were mainly intact.

Taking inspiration from the strengthening and stiffening observed for chemically-adhesive particles, we hypothesized that we could leverage dynamic and reversible chemical bond interactions to add additional stimuli responsiveness to MRF. Specifically, if the chemical adhesion of the particles could be modulated chemically, this could translate to large changes in the stiffness and strength of the solidified MRF on-demand. Thus, we synthesized tMRF, containing particles that were functionalized to present a thymine group on the particle surface suspended in a non-electrolytic solvent, anisole, instead of water as was used for pMRF. Alternative carrier fluids could be used depending on their compatibility with a given particle functionalization. In this case, without an additional linking molecule such as melamine, the particles are not expected to interact through hydrogen bonding. However, as melamine is able to form hydrogen bonds with multiple thymine moieties [36], the addition of melamine should induce the formation of hydrogen bonds between the thymine-functionalized particles in the tMRF (figure 5(a)). To explore this idea, two systems were prepared, tMRF without melamine and tMRF with melamine (tMRF + mel). In contrast with the pMRF system, requiring a linking molecule for bonding endowed the tMRF system with more tunability and stimuli-responsiveness.

Flow-mode and oscillation-mode rheology were performed for the thyme-based system in order to contrast its behavior to the pMRF. In figure 5(b), representative plots of \( \tau \) vs \( \gamma \) for the tMRF and tMRF + mel were included for \( B = 0.8 \) T and again fit to equation (1). In all cases, tMRF + mel exhibited higher \( \tau_0 \) than the tMRF and the percent increase is shown in figure 5(c) for \( \varphi = 2 \), 4, and 8 vol\%. As with the pMRF, the percent increase in \( \tau_0 \) was about 40\% for \( \varphi = 2 \) vol\% and decreased with increasing \( \varphi \), suggesting that the mechanism of strengthening was the same. Additionally, oscillation-mode measurements were conducted for \( \varphi = 2 \) vol\%, as shown in figure 5(d), and were used to calculate the difference in stiffness between tMRF and tMRF + mel. The plateau stiffness \( G_0^{+ \text{mel}} \) of tMRF with melamine was twice as large as the plateau stiffness \( G_0 \) of tMRF without melamine, in agreement with the comparison between pMRF and cMRF. Collectively, these results show that the tMRF + mel successfully maintained the same stiffening and strengthening as pMRF, but with a more flexible, dynamically linkable system.

While the main focus of this work is the determination of how adhesive coatings affect the fundamental magnetorheological properties of suspensions of magnetic particles, industrial MRF formulations for field use also include a series of additives designed to stabilize the magnetic particles to ensure that the MRF remains usable for months or years of operation [2, 9, 26]. Here, all MRF were prepared without additional additives in order to isolate the difference in performance due to the functionalization alone. The application of the principles uncovered in this study to commercial formulations...
of MRF would require further investigation to identify and optimize stabilizing agents that have chemical orthogonality to any adhesive coating.

Finally, in addition to $\tau_0$ and $G_0$, the off-state viscosity is another important design consideration for MRF-based devices. Thus, we sought to determine whether the addition of the adhesive coatings would increase the effective viscosity $\eta_{eff}$. Interestingly, our results were consistent with the adhesive coating leading to a slight increase in $\eta_{eff}$. Specifically, the phosphonate coating increased the low field $\eta_{eff}$ by $\sim 20\%$ (figure S1 (available online at stacks.iop.org/SMS/31/077001/mmedia)) while the addition of melamine increased the off-state $\eta_{eff}$ of tMRF, but not in a statistically significant manner (figure S2). Both of these results show that viscosity is not drastically increased, or even increased in a manner that is commensurate with the yield stress or stiffness increase, by the addition of the adhesive coating.

### 4. Conclusion

Taken together, this work shows the potential for increasing performance metrics and introducing tunability of MRF through responsive surface coatings. Specifically, the performance of MRF with chemically-adhesive particles was compared to the performance of MRF formed by non-adhesive particles. In brief, chemically-adhesive particles drastically stiffened the solidified MRF in a manner independent of $\phi$. While these coatings also strengthened MRF by as much as $40\%$, this strengthening decreased as the $\phi$ increased. We attributed this decrease to the topological change between isolated chains and BCT solids as $\phi$ increased. It should be emphasized that the fact that a small molecule can impart such a large change on the bulk performance of particles that are billions of times their mass showcases the importance of tuning particle surfaces. Beyond these implications, future work could explore ways to further tune the performance on-demand by slowly doping the linking molecule to modulate yield stress, or even through using a linking molecule that exhibits photoisomerization to allow the user to modulate adhesion with the application of light, as has been used to successfully assemble nanoparticles on-demand [37, 38]. In addition, this work highlights chemical tunability as an underutilized way in which to dynamically tune the properties of MRF and smart fluids more generally. Such chemical interactions could be utilized to locally tune the mechanics of MRF and even tune the temperature dependence of MRF properties.

### Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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