Tribology International 124 (2018) 124–133

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Synthesis and tribological testing of poly(methyl methacrylate) particles containing encapsulated organic friction modifier

Karen Mitchell[a,*], Anne Neville[a], Gary M. Walker[b], Michael R. Sutton[b], Olivier J. Cayre[a]

[a] Faculty of Engineering, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
[b] Lubrizol Limited, The Knowle, Nether Lane, Hazelwood, Derby, DE56 4AN, UK

ARTICLE INFO

Keywords:
Boundary
Lubricant additives
Particles

ABSTRACT

The tribological behaviour of polymer particles containing an encapsulated, organic friction modifier (FM) is presented. Particles comprising of a poly (methyl methacrylate) (PMMA) shall and a methanol core, into which FM was dissolved, were produced via a dispersion polymerization producing a core-shell morphology. The inclusion of these particles dramatically increased the overall concentration of FM which could be blended into dodecane.

The tribological behaviour of the particles produced, both with and without encapsulated FM, was tribologically tested in pure dodecane.

The addition of as little as 1.5 wt% particles was found to decrease the friction coefficient and measured wear volumes below those for dodecane saturated with FM. Data suggests that the FM delivery method may be dominated by a bursting mechanism.

1. Introduction

In a passenger car as much as 28% of the energy produced by a tank of fuel is used in overcoming frictional forces within the engine [1], with as little as 12% of the total energy being used to drive the wheels [2–4]. Pressure to increase fuel economy, reduce engine emissions, and increase the lifetime of engine parts has been growing over recent years and this has driven the development of new engine technologies and lubricants [2,5]. In order to optimise the lubricating performance of engine oils, and to allow engines to perform to the best of their ability, different chemical additives are blended into the oil. These additives can function either to enhance the lubricating performance of the base oil being used or to protect the metallic surfaces of the engine [5–8]. Of particular importance are the surface active additives, such as friction modifiers and antiwear additives, which help to improve the tribological performance in boundary/mixed lubricated systems. The main role of these additives is to interact with lubricated surfaces to produce a low friction, durable tribofilm [9]. During the extended periods of time between services, the additives will be depleted due to the normal operation of the oil in the engine; this results in a decrease in the effectiveness of the engine oil in reducing friction and wear between moving parts. Therefore, new methods must be developed to introduce fresh additives into the oil over time, potentially overcoming this issue. At present, the amount of additive that can be blended into an engine oil is dictated by the solubility of each additive into that oil and the desire to balance and control possible additive - additive interactions [10–15].

In this study, we use a microencapsulation system to increase the concentration of an organic friction modifier (FM) in a model oil. This is an innovative approach to increase the additive concentration of an engine oil, and also has the potential to replenish additive concentrations whilst in service.

Microencapsulation of active ingredients is a common solution adopted in a wide variety of industries, including the pharmaceutical, food, and dye industries among many others, and as such has been widely documented [16–18]. Reasons for microencapsulation can include, but are not limited to: protection of the core from chemical reaction, oxidation or degradation, protection from harsh environments or to allow the targeted, controlled release of an active ingredient from the microcapsule/particle core over a given time period or under specific conditions, including in response to certain triggers (for example, changes in temperature or pH) [19]. The particles prepared here are designed to act as an ‘additive reservoir’, capable of replenishing the additive concentration in the oil as it is consumed.

2. Additive microencapsulation process

The designed particles were prepared via dispersion polymerization

---

[*] Corresponding author. Robert McBride Ltd, West Carr Lane, Sutton Fields Industrial Estate, Hull, HU7 0BU, UK.
E-mail address: k.mitchell@mcbride.co.uk (K. Mitchell).

https://doi.org/10.1016/j.triboint.2018.04.009
Received 5 December 2017; Received in revised form 21 March 2018; Accepted 8 April 2018

in a non-aqueous continuous phase [20,21]. Dispersion polymerization typically results in the production of monodisperse, spherical polymer particles. Typically, spherical particles have a higher elasticity than irregularly shaped particles and are less likely to interact with surface asperities [22,23], this makes them highly suited for use in tribological applications. The general principle behind dispersion polymerization is that all reactants, including the monomer, are soluble in the reaction medium, but the corresponding polymer is insoluble and thus precipitates during the polymerization process (as the polymer grows to a longer chain length) and forms seed particles. These seeds then continue to grow until all of the monomer is consumed [24,25] or the polymerization is quenched. The use of polymeric stabilisers, the use of which is typical of non-aqueous dispersion polymerization processes, prevents particle aggregation throughout the polymerization process. These stabilizers locate themselves on the surface of the growing (and final) particles, providing colloidal stability in the continuous phase. In this particular work, we chose to use a stabilizer consisting of a reactive homopolymer (or macromonomer), which would participate in the polymerization reaction. This resulted in the growth of a second block onto the homopolymer stabilizer as the reaction proceeds, which anchors the stabilizer on the surface of the particles. This process, and the synthesis carried out in this work, are described schematically in Fig. 1.

To achieve a polymer particle with a liquid core, in which the FM will be encapsulated, a co-solvent, in our case methanol, is added to the initial polymerization mixture, as represented in Fig. 2. This co-solvent is incorporated within the particle core during the polymerization process as it preferentially wets the precipitating polymer rather than mixing with the dodecane continuous phase due to the very poor solubility of methanol in the dodecane [19,26,27].

For a successful co-solvent (and additive dissolved within the co-solvent) encapsulation process, the following conditions must be met:

- The continuous phase and co-solvent must be immiscible;
- The additive should be soluble in the co-solvent, but not in the continuous phase.

The organic FM used here was a commonly used NOCH (nitrogen, oxygen, carbon and hydrogen) additive with a chemical structure similar to that of standard surfactants. This may also contribute to its incorporation within the growing particle seeds. The polymer stabilizer has a greater affinity for the particle surface and thus the FM is thought to mostly be present within the core of the particles.

Particles produced were tested for colloidal stability over a period of months, and aside from obvious sedimentation over time as a result of density differences, no signs of significant aggregation were found in any samples. This was due to the use of PDMS layer present on the surface of the particles. This polymer layer is chemically anchored on the particle and fully solvated by the continuous phase, which provides a long-term steric layer on the particles preventing aggregation.

3. Experimental

3.1. Synthesis of solid poly(methyl methacrylate) particles

Particles were synthesized via dispersion polymerization in a non-aqueous continuous phase. The initial polymerization mixture used in the synthesis of the poly (methyl methacrylate) (PMMA) particles is detailed in Table 1.

Here, particle diameter and polydispersity were controlled by altering the concentrations of the various components (i.e., monomer concentration, initiator concentration etc.) or by changing the physicochemical characteristics of particle production process (i.e., stirring speed, reaction time etc.).

PDMS-MA, dodecane, AIBN and MMA were added, in this order, to a round bottom flask, which was then fitted to a condenser refluxer. The whole system was then purged with N_2(g), in an ice bath, whilst stirring at 300 rpm for 30 min using an overhead stirrer. Subsequently, the nitrogen source was removed and polymerization was carried out at 80 °C, 300 rpm for 4 h. Once polymerization was complete, air was let into the system, which degrades any free radicals remaining in the reaction medium, thus stopping the reaction. At this point, the warm particle suspension was filtered through a plug of glass wool to remove any aggregates that may have formed. Unreacted monomer and excess stabilizer were removed from the suspension through repeated cycles of centrifugation, removal of the supernatant and resuspension of the particles in fresh dodecane.

Particles synthesized by this method were highly monodisperse and could be synthesized in a controllable manner to the desired hydrodynamic diameter [21]. A Malvern Zetasizer Nano ZS was used to measure the hydrodynamic diameter and polydispersity of the resulting particle suspension. This was subsequently verified using electron microscopy.

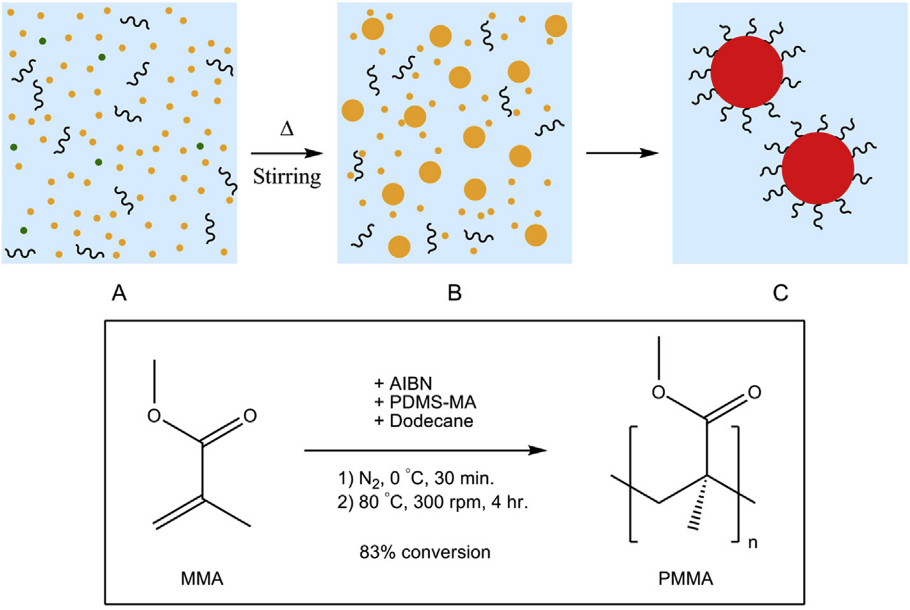

Fig. 1. A – Stabilizer (~), initiator (■) and monomer (orange ●) are dissolved in a continuous phase. B – Upon stirring and heating, monomers react and grow into precipitating polymer chains, primary particles form and grow in solution. C – When all of the monomer has reacted, polymerization is complete. Polymer particles (red ●) are prevented from aggregating by surface stabilizers. The reaction scheme shown below describes the reaction conditions and resulting monomer conversion. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

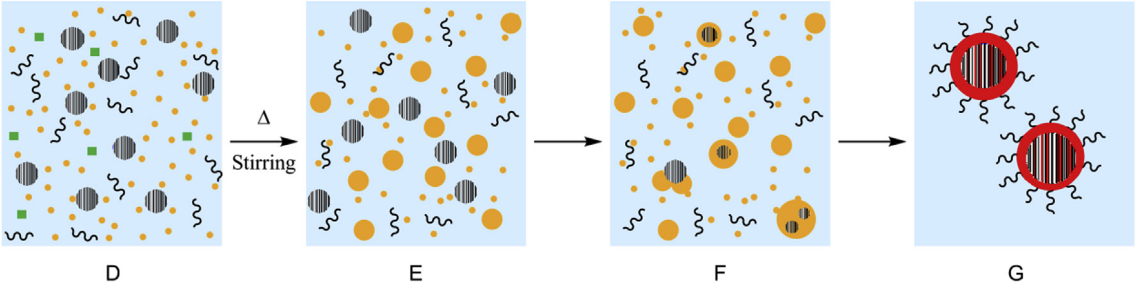

Fig. 2. Dispersion polymerization in the presence of the insoluble co-solvent methanol in which the FM is initially dissolved. D) Continuous phase (containing stabilizer - ~, initiator – ■ and monomer – orange ●) and a co-solvent (striped ●) are stirred and heated. E) Primary particles form in the continuous phase. F) Co-solvent incorporates within the growing polymer particles. G) Polymer particles (red ●) are formed containing encapsulated co-solvent. Stabilizers prevent particle aggregation during the polymerization process and provide stability to the final particle in the continuous phase. The typical conversion rate in this particular synthesis was measured to be ~70%. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Initial polymerization mixture.

Monomer	Methyl methacrylate (MMA) (2.5–22.0 wt% w.r.t. continuous phase)
Initiator	Azobisisobutyronitrile (AIBN) (0.72–5.2 wt% w.r.t. monomer)
Macromonomer Stabilizer	Methacrylate terminated poly (dimethyl siloxane) (PDMS-MA) (7.4–109 wt% w.r.t monomer)
Continuous phase	Dodecane

3.2. *Synthesis of poly(methyl methacrylate) particles with an encapsulated organic friction modifier within a methanol liquid core*

To prepare PMMA polymer particles with a liquid core, a co-solvent (methanol), which meets the criteria defined in section 2 above, is added to the initial polymerization mixture. Organic FM was dissolved in the methanol prior to starting polymerization with the aim of retaining the FM within the methanol core of the resulting particles. The dispersion polymerization process was carried out with a 9:1 ratio between the dodecane continuous phase and methanol. Synthesis was carried out as detailed in Section 3.1. And once again, unreacted monomer and excess stabilizer were also removed using repeated centrifugation and redispersion steps.

Particles prepared were highly monodisperse and could be synthesized in a controllable manner to the desired hydrodynamic diameter. The encapsulation of FM within the particles allowed for a much greater concentration of additive (up to 3.07 wt%) to be added to the dodecane than is possible using traditional blending methods (~0.004 wt%).

3.3. *Tribological testing*

Tribological testing was carried out using a Cameron Plint TE77, low speed reciprocating test machine. The TE77 tribometer uses a pin attached to a reciprocating arm which moves across a stationary plate.

Testing conditions were chosen to simulate the running conditions of the piston ring and cylinder liner system within an engine. The load, frequency and applied force were chosen to replicate boundary lubrication conditions. The radius of the pin, the materials of the pin and plate, and the roughness of both surfaces were also chosen to achieve boundary lubrication and to mimic the materials used within a typical engine. The TE77 operating temperature was chosen to be within the working range of the organic friction modifier whilst still being below the glass transition temperature of the PMMA used. The materials used and operating conditions are shown in Table 2.

The experimental work has been designed to evaluate the effect of particle type (with or without FM in the core), particle diameter and particle concentration on friction performance.

Wear analysis was conducted using scanning white light interferometry on a Bruker NP FLEX interferometer. All measurements were taken under vertical scanning interferometry mode, scan speed 1, magnification 2.5x.

Table 2
Cameron Plint TE77 schematic and test conditions for the specific experiments conducted in this work.

Pins	Cast iron (Ø 6 mm, radius 10 mm, 43–47 HRC)
Plates	AISI 52100 Steel (58–60 HRC)
Run Conditions	80 °C, 25 Hz, 24.5 N, 0.78 GPa

3.4. *Oil samples used in tribological testing*

The action of organic FM in model oils and fully formulated oils is well documented [22,23,28–31]. However, in our case, a model oil (i.e. dodecane) was used throughout this study, and due to this it was necessary to initially confirm the ability of our chosen FM to reduce friction and wear when dissolved in dodecane. Subsequently, this study will focus on the effect of the particles themselves on friction and wear of the system.

A testing matrix was thus devised to accommodate both of these aspects. These experiments were deisgned to investigate the friction and wear reduction properties of:

1) Dodecane, containing no engine oil additives or particles.
2) Dodecane fully saturated with FM. This represents the maximum concentration of FM which could be blended into the model oil through traditional blending methods.
3) Dodecane with solid PMMA particles containing no FM. Respectively, particles with diameters measuring ~150 nm (small), ~850 nm (medium) and ~1600 nm (large) were tested.
4) Dodecane with particles containing a methanol core, with no added FM.
5) Dodecane with particles containing a methanol core, with dissolved FM. These particles are referred to as 'FM-loaded' particles in this text. Here, particles measuring ~1000 nm in diameter were tested, which contained different concentrations of FM within their cores.

Information regarding the polydispersity index of the particles produced and used in this work can be found in the Supplementary Information. These are given alongside SEM micrographs of the particles as synthesized.

All of the different particle types were tested at different particle concentrations in order to study the corresponding effects on the friction and wear. It should be noted that, in samples that contained encapsulated FM, altering the particle concentration also altered the concentration of FM in the system. All particle samples were compared to pure dodecane (0 wt% particles) and also dodecane fully saturated with FM (0 wt% particles). To produce dodecane fully saturated with FM (0 wt% particles) incremental amounts of FM were weighed into the dodecane, at room temperature, until a saturated solution was reached. The solution was considered saturated at the appearance of a cloud point in the liquid. This particular method was chosen as it replicates the traditional method of blending additives into an engine oil and demonstrates that the low concentration of FM which can be blended into dodecane is representative of what can be incorporated into a fully formulated oil. The maximum amount of FM soluble in dodecane was estimated to be 0.004 wt% with this method.

4. Results & discussion

4.1. Effect of adding particles of different morphologies to dodecane

4.1.1. Friction

Here, the tribological behaviour of dodecane containing solid PMMA particles, PMMA particles with a liquid methanol core, and 'FM-loaded' PMMA particles with a liquid methanol core. Each sample is also compared to pure dodecane and dodecane fully saturated with FM. All testing was carried out using the test parameters detailed in Section 3.3 and was repeated at least three times.

Given a equilibration period of 30 min, it can be seen that the coefficient of friction for pure dodecane was one of the highest of any of the samples measured (Fig. 3). It also showed the largest fluctuation of any of the samples tested. As expected, when dodecane is fully saturated with FM, the friction coefficient measured is reduced and after an initial equilibrium period appears to reach a steady state.

The inclusion of PMMA particles does not appear to have an effect on the friction coefficients recorded when compared to that of pure dodecane. Dodecane samples containing particles with a methanol core but no FM appear to reduce the friction below that measured for pure dodecane although the difference observed is only clear after a running time of 80 min. These results do not show any significant effect of solid particles on friction reduction, which is to be expected as PMMA homopolymers are not known to have inherent friction reducing properties. While no conclusions can be drawn between pure dodecane and particles that do not contain any FM due to the size of the error seen, the comparison between pure dodecane and samples containing FM shows a marked decrease in friction coefficient. The sample of 'FM-loaded' particles suspended in dodecane showed the lowest friction coefficient of all samples, thus demonstrating a benefit in drastically increasing the FM concentration in the oil via this encapsulation process. The differences demonstrated in this initial figure are explored in greater details in the next sections.

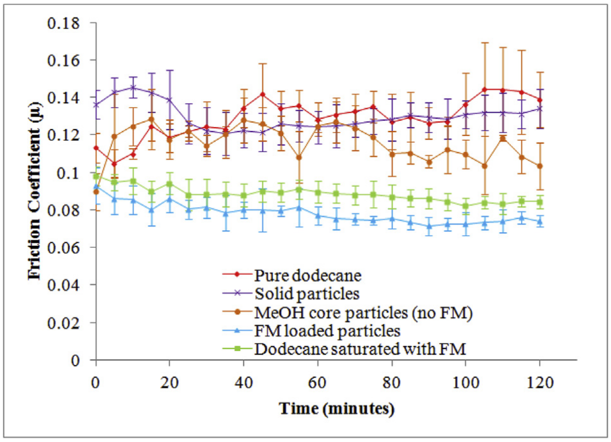

Fig. 3. Friction coefficient (µ) over a time period of 2 h. Pure dodecane (◆), dodecane saturated with FM (■), dodecane with solid PMMA particles (14 wt% particles) (**x**), dodecane with PMMA particles containing a methanol core but no FM (14 wt% particles) (●), and dodecane with 'FM-loaded' PMMA particles (14 wt% particles) (▲). Each plot is the average of three separate tests, carried out under identical conditions, error bars are the standard deviation of the three tests and lines are plotted to guide the eye.

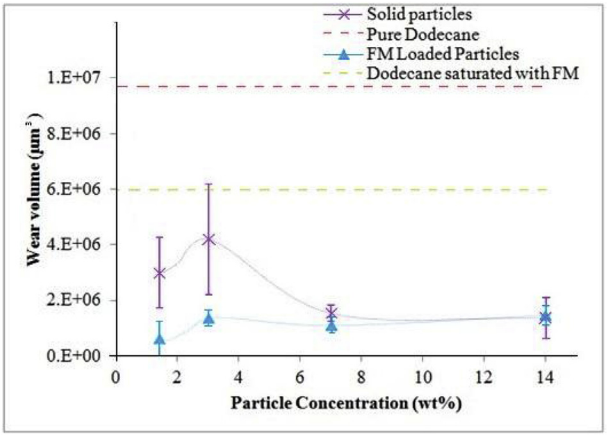

Fig. 4. Wear volume (μm^3) of the steel plates after the 2-h test period. Pure dodecane (horizontal dotted line $[\sim 9.7 \times 10^6\ \mu m^3]$), dodecane with solid particles (**x**), dodecane saturated with FM (horizontal dotted line $[\sim 5.9 \times 10^6\ \mu m^3]$), and dodecane with 'FM-loaded' particles (▲) (14 wt% particles is equivalent to 3 wt% FM in the overall sample; 7 wt% particles = 1.5 wt% FM; 4 wt% particles = 0.8 wt% FM; and 1 wt% particles = 0.3 wt% FM). Each plot is the average wear volume measured for three separate test plates, carried out under identical conditions, error bars are the standard deviation of the three tests and lines are plotted to guide the eye.

4.1.2. Wear

Wear tests were conducted on the same steel plates used in the TE77 testing as described in the experimental section. The corresponding data is shown in Fig. 4. Each result is the average wear volume measured for the three separate plates, where testing was carried out under identical conditions.

As expected, it is clear that a FM-saturated dodecane leads to a noticeable reduction in wear volume when compared to pure dodecane. Furthermore and more interestingly, for both sets of particles (solid PMMA particles and 'FM-loaded' particles) the measured wear volume was lower than that measured when no particles were incorporated into the dodecane. This was true at all particle concentrations. The effect of changing the concentration of solid particles follows no specific trend although for FM-loaded particles, the wear volume appears to be within experimental error for all particle concentrations. Consequently, it can be seen that only a small amount of the solid PMMA particles needs to be dispersed into dodecane in order to produce a dramatic reduction in the wear volume.

The wear scars resulting from these experiments were analyzed using scanning white light interferometry, which also allows for scar depth to be measured. Fig. 5 shows a comparison between wear scars generated when pure dodecane and FM-saturated dodecane are used as lubricating oils.

Organic friction modifiers and antiwear additives are both surface active additives and operate under similar conditions, which is likely to contribute to the organic friction modifier used in this study also having some mild antiwear properties [12]. As expected, the depth of the wear scar when FM-saturated dodecane is used (~1.1 µm) is much smaller than in the case of pure dodecane (~4.7 µm). This confirms that the FM acts as it should when dissolved in dodecane, retaining the significant desired effect on the surface wearing process.

Examples of the wear scars seen for dodecane containing solid particles (14 wt%) and those generated for dodecane containing 'FM-loaded' particles (14 wt% particles, equivalent to 3 wt% FM) are shown in Fig. 6 and Fig. 7, respectively. The wear scars here are much shallower than when pure dodecane (~4.7 µm) was used as a lubricating

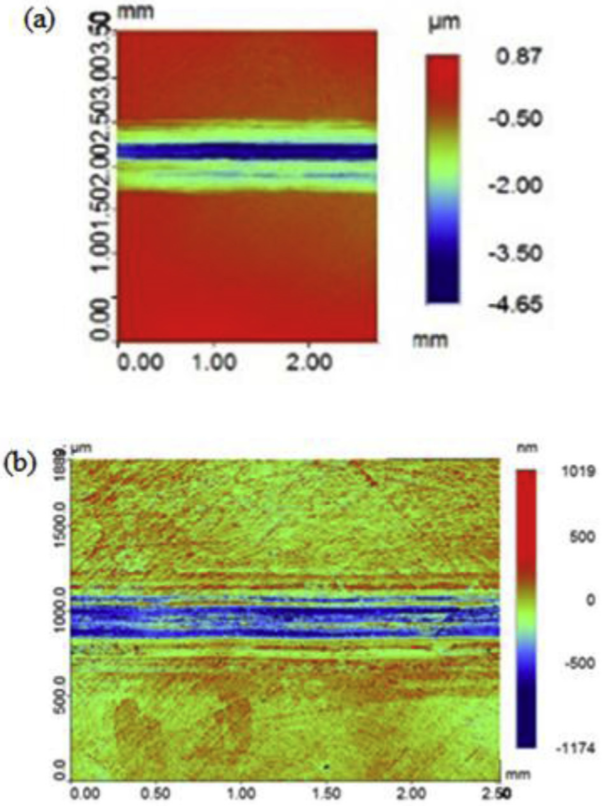

Fig. 5. (a) Depth of wear scars on a steel plate tested when dodecane is used as a lubricating oil and (b) when dodecane fully saturated with FM (0.004 wt%) is used as a lubricating oil in TE77 testing.

oil. The wear scar generated when using dodecane with solid particles appears deeper (~0.45 µm) and better defined than the wear scar imaged when dodecane with the FM-loaded particles (~0.10 µm) were used as a lubricating oil.

Samples containing particles showed an 84% reduction in wear when compared to plates tested with fully saturated dodecane, and an 89% reduction in wear compared to plates tested in pure dodecane (Fig. 5). There appears to be very little variance between samples of different particle concentration, which again shows that only a small percentage of particles need to be incorporated into dodecane to produce the desired reduction in wear.

At most particle concentrations, the particles containing encapsulated FM produced lower wear during testing than when solid particles were used. This suggests that there is a synergy between FM and the PMMA used to form the particle shell, which results in unique wear reducing properties.

4.2. Effect of particle diameter

4.2.1. Friction

The 2-h friction tests were considered to have reached a steady state during the last 30 min of the test, at this point the running-in period was complete. The friction coefficients during this steady state period are thus averaged out for each sample and are given in Fig. 8. Each result is an average of the three separate tests and the error bar for each data point corresponds to the standard deviation of these three tests. The particle samples that were used to determine the effects generated by particles of different sizes were all solid PMMA particles, which contained no FM. The solid particles possessed average diameters of approximately 1600 nm, 850 nm and 150 nm, respectively. It is worth noting that the stated friction coefficients for pure dodecane, and dodecane saturated with FM, are for comparison only and contain no particles.

As expected, blending the FM into dodecane produces a friction coefficient (0.0084 ± 0.003) lower than that measured for the dodecane itself (0.139 ± 0.015).

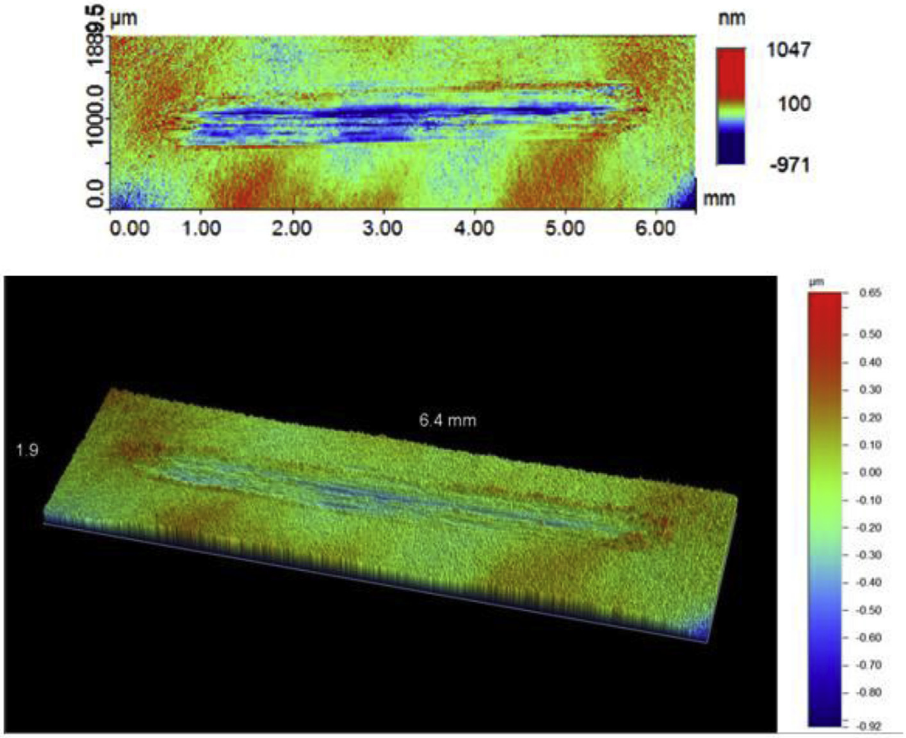

Fig. 6. 2D and 3D interferometry images of the wear scar of a steel plate tested when dodecane with solid particles (14 wt% particles) is used as a lubricating oil.

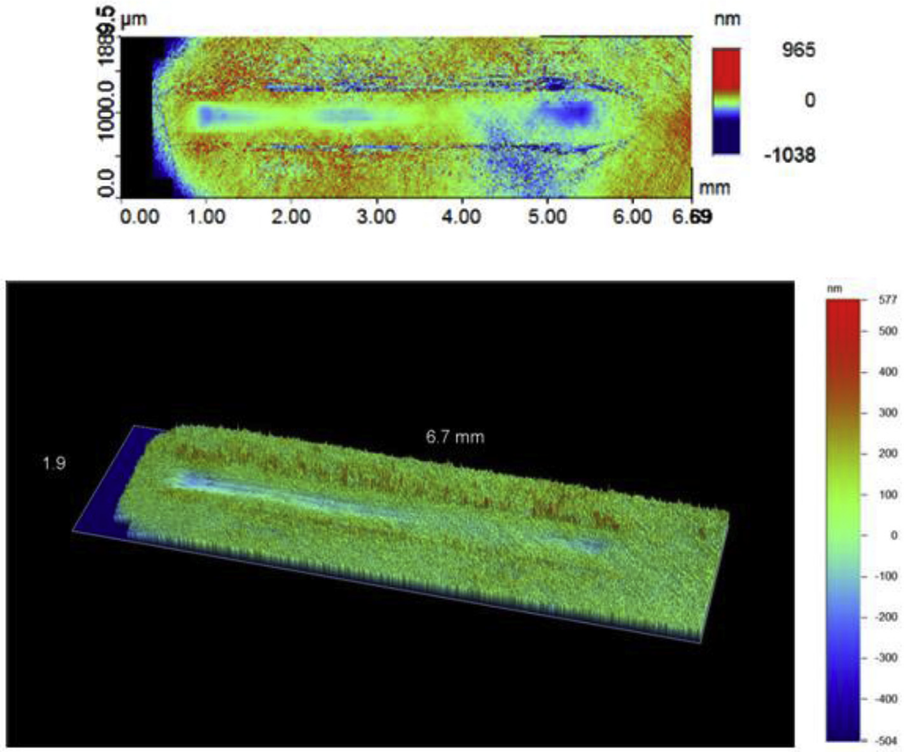

Fig. 7. 2D and 3D interferometry images of the wear scar of a plate tested when dodecane with FM-loaded particles (14 wt% particles; 3 wt% FM) was used as a lubricating oil in TE77 testing. In this case the wear scar created during testing was not fully centered (as can be seen from the dark area on the left of the plate on the top image). This experimental variation was taken into account when determining the wear volumes from image analysis.

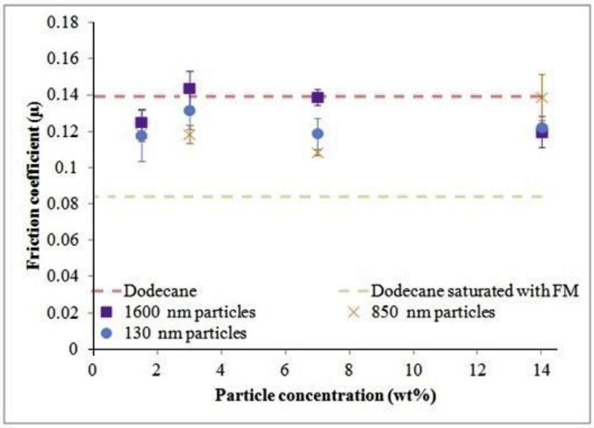

Fig. 8. Friction coefficient (µ) during the last 30 min of the 2 h tests, error bars coloured for clarity. Pure dodecane (upper horizontal red dotted line, friction coefficient = 0.139), dodecane with 1600 nm solid PMMA particles (■, purple), dodecane with 850 nm solid PMMA particles (**x**, orange), dodecane with 150 nm solid PMMA particles (●, blue), and dodecane saturated with FM (lower horizontal green dotted line, friction coefficient = 0.084). Here, all particles are solid PMMA particles and do not contain any encapsulated FM. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

At all particle concentrations tested, the measured coefficient of friction is higher than those measured for the FM-saturated dodecane. The effect of changing the concentration of solid particles used appears not to follow a trend. As a result, there was little evidence found to support a clear link between the particle concentration and the measured friction. This observation again highlights that the addition of only a small concentration of particles is necessary to improve reliability and friction reduction. A small increase in friction coefficient was seen for the largest particle diameter but without being statistically significant. As there is no great advantage to using any particular particle diameter investigated here, future applications may emphasize the final appearance of the oil as a deciding factor in incorporating particles within the lubricant formulations, as particles above 100 nm may result in cloudy oils as they scatter light efficiently.

Each sample was tested at the same particle concentrations but, because of the differing particle diameters, each sample also contained a different number of particles. Over the range studied, it seems that the number of particles (and therefore the corresponding total particle surface area in the sample) in the system does not have a direct effect on the friction coefficient measured, as shown in Fig. 9.

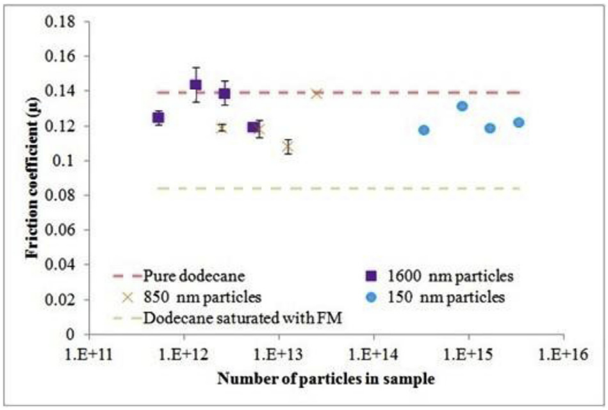

Fig. 9. Friction coefficient (µ) during the last 30 min of the 2 h tests versus number of particles in the sample. Pure dodecane (upper horizontal red dotted line, friction coefficient = 0.139), dodecane with 1600 nm solid PMMA particles (■, purple), dodecane with 850 nm solid PMMA particles (**x**, orange), dodecane with 150 nm solid PMMA particles (●, blue), and dodecane saturated with FM (lower horizontal green dotted line, friction coefficient = 0.084). Here, all particles are solid PMMA particles and do not contain any encapsulated FM. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

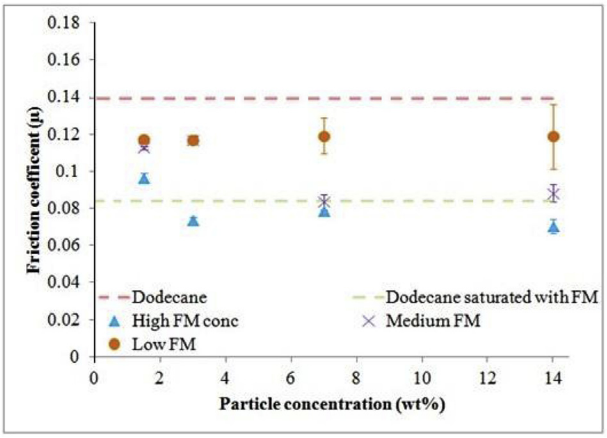

Fig. 10. Friction coefficient (μ) during the last 30 min of the 2 h tests, error bars coloured for clarity. Pure dodecane (upper red horizontal dotted line, friction coefficent = 0.139), dodecane with 1100 nm 'low' 'FM-loaded' particles (●, orange) (1 wt% particles is equivalent to 0.1 wt% FM; 3 wt% particles = 0.2 wt % FM; 7 wt% particles = 0.4 wt% FM; and 14 wt% = 0.7 wt% FM), dodecane with 900 nm 'medium' 'FM-loaded' particles (x, purple) (1 wt% particles = 0.1 wt% FM; 3 wt% particles = 0.4 wt% FM; 7 wt% particles = 0.7 wt% FM; and 14 wt% particles = 1.5 wt% FM), dodecane with 1100 nm 'high' 'FM-loaded' particles (▲, light blue) (1 wt% particles = 0.3 wt% FM; 3 wt% particles = 0.8 wt% FM; 7 wt% particles = 1.5 wt% FM; and 14 wt% particles = 3.1 wt% FM), and dodecane saturated with FM (lower green horizontal dotted line, friction coefficient = 0.084). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

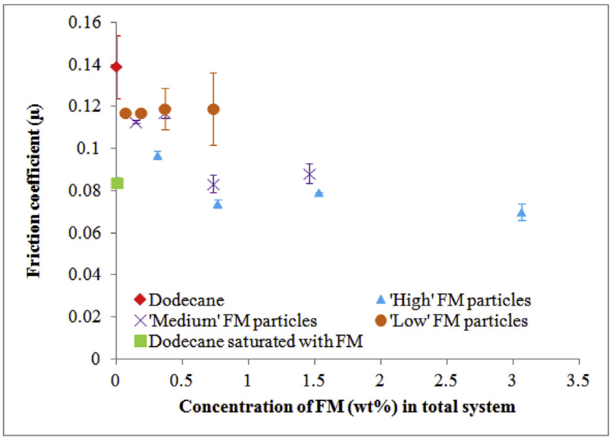

Fig. 11. Friction coefficient (μ) during the last 30 min of the 2 h tests, error bars coloured for clarity. Dodecane with 'FM-loaded' particles. Particle concentrations correspond to the samples shown in Fig. 10.

4.3. *Effect of changing FM concentration encapsulated in particles*

4.3.1. *Friction*

As seen in Fig. 10, 'FM-loaded' particles appear to have the potential to reduce the measured coefficient of friction below that of dodecane fully saturated with FM, which here represents the amount of FM that could be blended traditionally. This suggests that the interaction of FM with the surface can be enhanced when the FM is encapsulated within the PMMA particles present in these samples. On this basis, the effect of the concentration of FM within the particles was also investigated to understand whether further decreases in friction coefficient could be recorded. For this purpose, particles were synthesized as detailed in Section 3.2 using varying amounts of FM. It should be noted that in the following tests, altering the particle concentration also directly alters the FM concentration within the overall system.

All samples containing particles with encapsulated FM produced friction coefficients below those measured for pure dodecane (0.139 ± 0.015). The effect of changing the concentration of particles used appears to follow no trend and, once again, there is little evidence in these samples to suggest that changing the concentration of particles used had a significant effect on the friction measured.

The particles containing the highest concentrations of FM encapsulated within their cores resulted in the lowest friction coefficient measurements, including cases where the friction coefficient was reduced to values below those measured in the fully saturated dodecane (0.0084 ± 0.003). This phenomenon is likely due to the fact that all of oil samples containing 'FM-loaded' particles have an FM concentration much higher than can be blended by conventional means. When comparing the 3.5 wt% and 14 wt% particle samples only a small change in friction is seen, suggesting that only a relatively small concentration of particles is needed to reduce friction. The need for only a low concentration of particles to be present in a lubricating oil should ensure that there is little effect on the appearance of the oil itself.

The amount of FM encapsulated does seem to have an influence on the friction coefficient measured. Fig. 11 shows the effect FM concentration has on the measured coefficient of friction.

Changing the concentration of particles in the dodecane produces a change in the concentration of FM in the system being tested, and, consequently, some of the different samples tested contained the same overall FM concentration. Despite these systems containing the same amount of FM, the particles that contain the most FM within their cores still produce the lowest friction coefficients, once again demonstrating that the number of particles does not have a direct effect on the friction coefficient measured.

Fig. 11 Indicates that the inclusion of a lower concentration of particles containing a high amount of encapsulated FM, can produce lower friction coefficients than a high concentration of particles containing a low amount of FM (i.e. where both samples have the same overall FM concentration in the system). This suggests that the delivery method of the FM may be dominated by the bursting of particles and the quick delivery of FM wherever and whenever it is needed, rather than the slow leaching of FM from the particles over time as was the initial hypothesis.

4.3.2. *Wear*

Fig. 12 shows the wear results obtained from particles containing different concentrations of FM encapsulated within their cores. Each result is the average wear volume measured of three separate plates, tested under identical conditions.

At all particle concentrations measured, the volume of wear was lower than for the experiments using pure dodecane only (~$9.7 \times 10^6 \pm 4 \times 10^5$ μm^3) and also for those testing dodecane fully saturated with FM (~$5.9 \times 10^6 \pm 7 \times 10^5$ μm^3). The effect of changing the concentration of particles, and thus the concentration of FM in the system, follows no specific trend. There appears to be very little difference between particles containing the various concentrations of FM and also little variance between samples of different particle concentrations. This suggests that while the organic friction modifier used may exhibit some mild antiwear properties, this effect has reached a maximum at some point and the presence of additional FM in the system provides no further advantage to the wear reduction seen. Once again, it can be seen that only a small amount of these 'FM-loaded' particles are needed in order to dramatically reduce the wear volume.

4.4. *Proposed mechanism of friction reduction*

Literature suggests that there are two general mechanisms of action when inorganic particles are used, either as an additive or as a solid lubricant, in a lubricant oil: a) a tribofilm is formed at the surface of the contacts or b) the particles act as rolling bearings in order to physically

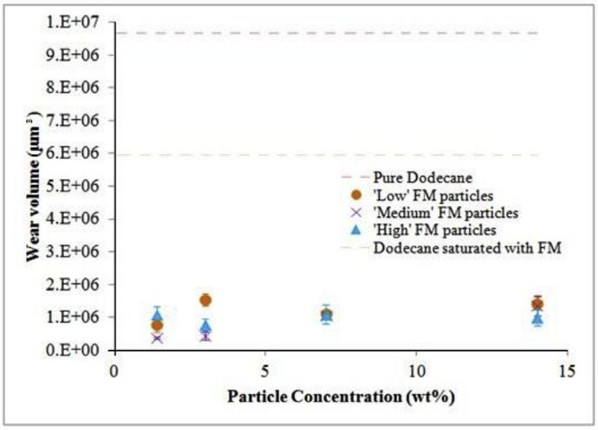

Fig. 12. Wear volume (μm^3) of the steel plates after the 2 h test period. Pure dodecane (horizontal dotted line [$\sim 9.7 \times 10^6$]) (off y-axis scale), dodecane with 'low' 'FM-loaded' particles (●, orange), dodecane with 'medium' 'FM-loaded' particles (**x**, purple), and dodecane with 'high' 'FM-loaded' particles (▲, blue). Each plot is the average wear volume measured of three separate test plates, carried out under identical conditions. It should be noted that the concentration of friction modifier as the concentration of particles changes. FM concentrations for each sample are as stated for Fig. 10. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

separate the surfaces [22,30–44]. While a number of mechanisms of friction reduction and wear reduction are proposed in these same studies, care must be taken in applying these to the particle system tested in this study. Mechanisms proposed in literature are focused on metallic-based nanoparticles with the majority being used in the elastohydrodynamic regime [33,45]. Particles in these studies were generally measured at particle concentrations [45,46] lower than 0.1 wt% to overcome the problem of particle aggregation. This problem is overcome here by the use of steric stabilisers incorporated onto the particles surface.

Tribological testing conditions chosen in this study were designed to produce boundary lubrication. It has been shown here that the addition of a relatively small concentration of PMMA particles in dodecane is enough to dramatically reduce the friction coefficient measured.

4.4.1. Scanning electron microscopy of the tribotested steel plates

After TE77 testing was complete, SEM was carried out on the steel plates used in the tribological tests to monitor the presence of a polymer film inside the wear scar. The SEM micrographs produced in this work have been provided in the Supplementary Information, Fig. S4 – S9. When exposed to the beam of electrons in electron microscopy chamber, PMMA will cross link and become damaged, thus changing the appearance of the polymer. Here, this phenomenon has been used advantageously to confirm the presence of a PMMA film; focusing the electron beam in one area long enough for damage to occur to the polymer produces an area that appears darker than its surroundings due to a build-up of charge. SEM analysis of the plates showed the creation of these darker areas inside the wear scar all along the length of the scar, but these were not created at any point outside of the wear scar; thus, making it clear that a PMMA tribofilm is formed in the wear scar during testing but nowhere else on the surface. The PMMA tribofilm only forms in the area of the contact suggesting that the formation of this tribofilm is directly due to the action of the contact between the pin and plate. The formation of this PMMA tribofilm may also account for the wear reduction seen when comparing samples with particles to samples without particles. This effect has been noted previously [44,47–50] and is characterized by the deposit of nanoparticles on the rubbing surfaces compensating for the loss of asperity roughness.

Plots of friction coefficient versus particle concentration, both of solid particles and FM-loaded particles, appeared to show a drop in friction coefficient at two different particle concentrations (3.5 wt% and 14 wt%). This suggests that there may be different friction reduction mechanisms taking place dependent on the concentration of particles present in the dodecane.

Through comparison of the wear scars in the samples tested, a mechanism for the formation of the tribofilm can be proposed. In the plates tested using pure dodecane (0 wt% particles) the direction of rubbing could be clearly seen. The plates supplied have a known roughness, which means that before testing is carried out some scratches due to polishing can be seen on the surface of the plates. These imperfections, present on the surface of the material before tribological testing, can still be seen outside the wear scar but were removed by the reciprocating action of the pin moving across the surface of the plate during the creation of the wear scar. Wear particles, characterized by their irregular shape and size (unlike the monodisperse, PMMA particles that are spherical), can be seen across the plate. The majority of these wear particles are found close to the wear scar.

At 1.5 wt% solid particle concentration in dodecane the polymer film formed inside the wear scar was not complete and intact PMMA particles could be seen outside the wear scar trapped in the scratches on the surface. Kao and Lin also reported this observation when using titanium dioxide particles [51].

When 3.5 wt% solid particles in dodecane were tested, a complete polymer tribofilm forms; this was confirmed by the disappearance of the polishing marks on the surface of the sample, and the lack of PMMA particles in the wear scar. This suggests that asperities on the surface were completely smoothed out by particles that had become trapped and crushed in the contact, smoothing the surface to produce a flat PMMA tribofilm.

When the particle concentration was increased up to 14 wt% in dodecane, a complete PMMA tribofilm could be seen inside the wear scar and was confirmed by the systematic damaging of the surface by the electron beam in SEM analysis. Outside of the wear scar, intact PMMA particles could be found across the surface, but once again no damage could be caused to the surface by the electron beam as no polymer tribofilm had formed there.

In each case, wear debris could be seen mixed with intact polymer particles closer to the wear scar, suggesting that some wear of the plate occurs before the formation of a protective polymer tribofilm. Further testing would need to be carried out to determine whether this is indeed the case. The drop in friction coefficient at higher particle concentration may therefore be due to the formation of a PMMA film working alongside a further friction reducing mechanism deriving from these intact particles.

In the literature, there are many theories that have been suggested as to the mechanism taking place at higher concentrations of particles, all of which focus on the physical separation of the two sliding surfaces due to the action of the particles [34–36,49]. A number of the studies of metallic nanoparticles suggest that a rolling mechanism may be taking place alongside film formation [51]. However, this is unlikely to be the case here as the polymer particles do not have sufficient mechanical strength to support the load applied.

4.4.2. Formation of polymer tribofilm

In all cases, the addition of particles reduced both the friction coefficient and measured wear volume when compared to both pure dodecane (0 wt% particles) and dodecane fully saturated with FM (0 wt% particles). SEM analysis has successfully been used to confirm the formation of a polymer tribofilm within the wear scar. Similar mechanisms were previously suggested, but not proven, for ZDDP coated metallic-core nanoparticles by Li et al. [52] and also by Hu et al. [35] for lanthanum borate particles. A similar mechanism has also been shown by Cizaire et al. [43], whereby inorganic IF-MoS_2 nanoparticles used in a lubricating oil were squeezed through a contact to create a tribofilm at the interface; the tribofilm itself then acting as a sacrificial

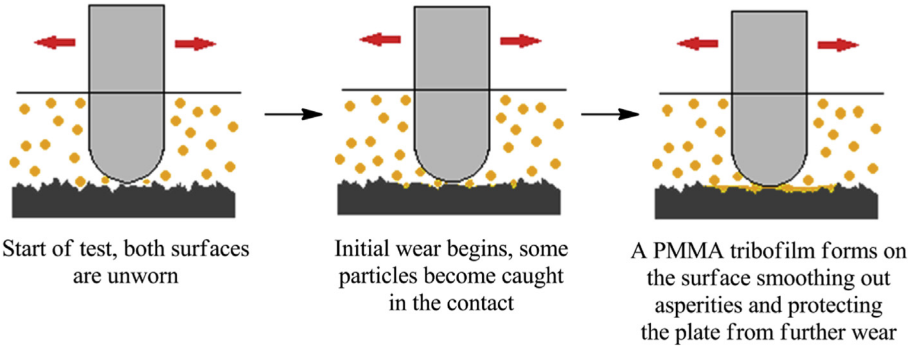

Fig. 13. Proposed mechanism of friction and wear reduction in samples containing solid particles.

FM/AW layer. The mechanism proposed here suggests that the PMMA particles may act in a similar fashion, however, the PMMA tribofilm is aided by the organic FM present in the system. An excellent overview of the separate possible mechanisms which may arise from the incorporation of either polymer nanoparticles or metallic nanoparticles, which themselves act as friction modifiers, has been given by Tang and Li [47]; we propose that a combination of these mechanisms may be in effect in our system due to the unique combination of an organic friction modifier being encapsulated within a polymeric nanoparticles.

A schematic of the proposed mechanism of friction and wear reduction of the particle samples tested in this work is shown in Fig. 13.

It has been demonstrated that the reduction of friction is linked to the amount of FM encapsulated within the core of the particle present in the dodecane model oil being tested; particles with higher concentrations of FM encapsulated within the core exhibited the greatest decrease in friction. This suggests that the delivery method of FM into the surrounding dodecane may be dominated by the bursting of particles which can quickly deliver the FM to where and when it is needed within the contact.

The mechanism by which organic FM layers are formed is well documented, but in samples of dodecane with 'FM-loaded' particles, a different mechanism appears to be observed. In the case presented here, it is anticipated that the FM self-assembles to form a tribolayer on the surface, possibly through hydrogen bonding with the polymer film. Other FM molecules then align depending on the polarities of the uppermost layer of FM, to form a protective multilayer, which is characteristic of organic FMs. This multilayer protects the metallic surface by acting as a sacrificial layer, which is removed by the action of the pin moving across the surface of the plate, resulting in free FM in the dodecane continuous phase. This FM then readheres to the surface to reform the tribolayer, shown in Fig. 14.

This work shows the potential of particles to release FM though a bursting mechanism. However, the particles also have the potential to act as an 'additive reservoir', capable of slowly leaching the FM into the oil over the lifetime of that oil.

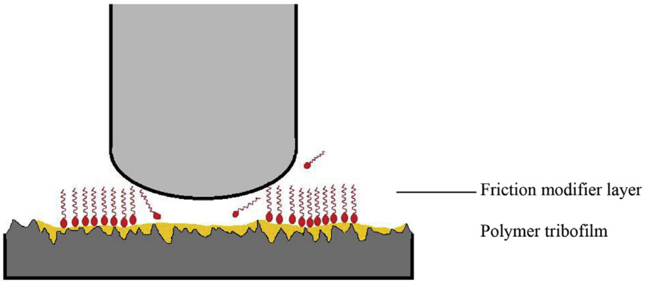

Fig. 14. Proposed mechanism of friction and wear reduction in samples containing FM-loaded particles. It should be noted that the polymer tribofilm and FM layer are likely to form on the surfaces of both the plate and the pin, for clarity this process is only shown on one surface here.

To demonstrate slow release, dodecane samples containing the 'FM-loaded' particles were centrifuged, the dodecane supernatant was removed and fresh dodecane was added to the particles, which were then gently re-suspended for the remainder of the test cycle. The supernatant dodecane was then tested by HPLC (high performance liquid chromatography) to determine the concentration of FM that was released into the continuous phase in one test cycle. Two cycle times were tested: 1 h, which ensured that the greatest concentration possible of FM had diffused into the dodecane, and 15 min, the shortest time period possible in which this testing could be carried out. Release data for the diffusion of FM from the core of the 'FM-loaded' particles into fresh oil is shown in Fig. 15. This data shows the ratio of FM cumulatively released into fresh dodecane as a function of cycle number.

It is clear that not all FM incorporated within the particle synthesis mixture has been encapsulated, as the cumulative release appears to plateau around a value of 35% of released FM (when compared to the total mass of FM included in the particle synthesis procedure). Some FM will preferentially remain in the particle core as a result of methanol being present within the particles. The cycle timescale (1 h or 15 min) does not appear to significantly alter the data, and therefore a longer experiment was run with the 15 min cycles, showing a steady state release of the FM after between 5 and 10 cycles. It can thus be seen that the 'FM-loaded' particles are able to fully replenish the FM concentration of the surrounding dodecane quickly and efficiently for both timescales. This demonstrates that the particles are capable of supplying the additive via this method for the lifetime of the oil in our experiments.

In reality a mixture of both additive replenishment methods described here may take place within a fully formulated oil in an engine.

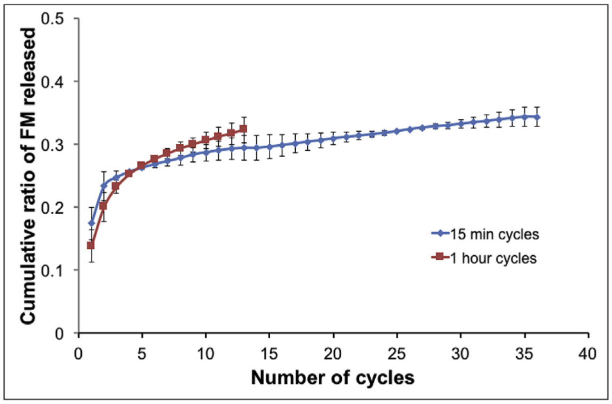

Fig. 15. Cumulative sustained release of FM with each cycle. Here, "cycle" refers to the amount of time the particles were redispersed in each aliquot of fresh dodecane.

5. Conclusions

This study has demonstrated that the encapsulation of an organic FM, by use of a co-solvent, is possible via dispersion polymerization in a non-aqueous continuous phase.

The effects of particle concentration, diameter, morphology, and the degree of 'FM-loading' within the PMMA particles on the friction and wear reducing properties of dodecane have all been investigated in this study. It has been found that adding particles to a dodecane model oil, either solid PMMA particles, PMMA particles with a methanol core, or 'FM-loaded' PMMA particles, can decrease the friction coefficient below that of pure dodecane, and in some cases can even decrease the friction coefficient below those measured for dodecane that has been saturated with FM via traditional blending methods. It has also been demonstrated that the addition of particles, of any type described here, can reduce the measured wear volumes when compared with pure dodecane or the dodecane fully saturated with FM. The effects of friction and wear reduction can be seen with the addition of only 1.5 wt% concentration of particles. This suggests that the delivery method of the FM may be dominated by the bursting of particles and the quick delivery of FM to wherever and whenever it is needed, rather than the slow leaching of FM from the particles over time as was the initial hypothesis.

A mechanism for friction and wear reduction has been proposed by SEM analysis of the steel plates that had been used in the tribological testing. When exposed to an electron beam, such as that in scanning electron microscopy, PMMA will cross-link and become damaged, thus appearing darker in the image taken. This phenomenon has been used to confirm the presence of a polymer tribofilm inside the wear scar after testing. This same phenomenon cannot be demonstrated outside of the wear scar, indicating that the tribofilm is only formed when particles enter the tribological contact and are broken by the action of the cast iron pin sliding across the steel plate. Accordingly, this means that the polymer tribofilm cannot be formed outside of the wear scar.

Acknowledgments

The authors wish to thank the EPSRC and The Lubrizol Corporation for funding of this project.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.triboint.2018.04.009.

References

[1] Holmberg K, Andersson P, Erdemir A. Global energy consumption due to friction in passenger cars. Tribol Int 2012;47(0):221–34.
[2] Tung SC, McMillan ML. Automotive tribology overview of current advances and challenges for the future. Tribol Int 2004;37(7):517–36.
[3] Taylor CM. Automobile engine tribology design considerations for efficiency and durability. Wear 1998;221(1):1–8.
[4] Priest M, Taylor CM. Automobile engine tribology approaching the surface. Wear 2000;241(2):193–203.
[5] Haque T, Morina A, Neville A. Influence of friction modifier and antiwear additives on the tribological performance of a non-hydrogenated DLC coating. Surf Coating Technol 2010;204(24):4001–11.
[6] Komvopoulos K, et al. Antiwear properties of blends containing mixtures of zinc dialkyl dithiophosphate and different detergents. Tribol Trans 2008;52(1):73–85.
[7] Bearchell CA, et al. Overbased detergent particles: Experimental and molecular modelling studies. Phys Chem Chem Phys 2001;3:4774–83.
[8] Vipper AB, et al. Antifriction action of lubricant additives. Lubric Sci 1995;7(3):247–59.
[9] Morina A, Zhao H. Surface analysis and tribochemistry of automotive engine components. In: Tung GTS, editor. ASTM lubrication handbook - automotive Lubricants and testing ASTM international. New York: SAE International; 2012. p. 351–78.
[10] Spikes HA. Additive-additive and additive-surface interactions in lubrication. Lubric Sci 1989;2(1):3–23.
[11] Unnikrishnan R, et al. Additive-additive interaction: an XPS study of the effect of ZDDP on the AW/EP characteristics of molybdenum based additives. Wear 2002;252(3–4):240–9.
[12] Sarin R, et al. Additive-additive interactions: search for synergistic FM-EP-AW composition. Wear 1994;174(1–2):93–102.
[13] Ramakumar SSV, Rao AM, Srivastava SP. Studies on additive-additive interactions: formulation of crankcase oils towards rationalization. Wear 1992;156(1):101–20.
[14] Sarpal AS, et al. Study of additive-additive interactions in a lubricant system by NMR, ESCA, and thermal techniques. Lubric Sci 2005;17(3):319–45.
[15] Neville A, et al. Compatibility between tribological surfaces and lubricant additives. How friction and wear reduction can be controlled by surface/lube synergies. Tribol Int 2007;40(10–12):1680–95.
[16] Nelson G. Application of microencapsulation in textiles. Int J Pharm 2002;242(1â€“2):55–62.
[17] Arshady R. Microcapsules for food. J Microencapsul 1993;10(4):413–35.
[18] Freiberg S, Zhu XX. Polymer microspheres for controlled drug release. Int J Pharm 2004;282(1–2):1–18.
[19] Yow HN, Routh AF. Formation of liquid core-polymer shell microcapsules. Soft Matter 2006;2(11):940–9.
[20] Barrett KEJ. Dispersion polymerisation in organic media. Br Polym J 1973;5(4):259–71.
[21] Richez AP, et al. Dispersion polymerisation in non polar solvent: evolution towards emerging applications. 2013.
[22] Wu YY, Tsui WC, Liu TC. Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. Wear 2007;262(7–8):819–25.
[23] Rapoport L, et al. Inorganic fullerene-like material as additives to lubricants: structure - function relationship. Wear 1999;225–229:975–82. Part 2(0).
[24] Klein SM, et al. Preparation of monodisperse PMMA microspheres in nonpolar solvents by dispersion polymerization with a macromonomeric stabilizer. Colloid Polym Sci 2003;282(1):7–13.
[25] Pelton R, Osterroth A, Brook MA. Silicone stabilized poly(methyl methacrylate) nonaqueous latex: 2. Flocculation by degradation of the steric layer. J Colloid Interface Sci 1991;147(2):523–30.
[26] Okubo M, et al. Production of micron-sized monodispersed core/shell polymethyl methacrylate/polystyrene particles by seeded dispersion polymerization. Colloid Polym Sci 1997;275(8):797–801.
[27] Loxley A, Vincent B. Preparation of poly(methylmethacrylate) microcapsules with liquid cores. J Colloid Interface Sci 1998;208(1):49–62.
[28] Leshchinsky V, et al. Behavior of solid lubricant nanoparticles under compression. J Mater Sci 2004;39(13):4119–29.
[29] Rapoport L, et al. Polymer nanocomposites with fullerene-like solid lubricant. Adv Eng Mater 2004;6(1–2):44–8.
[30] Sunqing Q, Junxiu D, Guoxu C. A review of ultrafine particles as antiwear additives and friction modifiers in lubricating oils. Lubric Sci 1999;11(3):217–26.
[31] Zhou J, et al. Tribological behavior and lubricating mechanism of Cu nanoparticles in oil. Tribol Lett 2000;8(4):213–8.
[32] Hernández Battez A, et al. CuO, ZrO_2 and ZnO nanoparticles as antiwear additive in oil lubricants. Wear 2008;265(3–4):422–8.
[33] Chinas-Castillo F, Spikes HA. Mechanism of action of colloidal solid dispersions. Transactions of the ASME 2003;125:552–7.
[34] Chen S, Liu W. Oleic acid capped PbS nanoparticles: synthesis, characterization and tribological properties. Mater Chem Phys 2006;98(1):183–9.
[35] Hu ZS, et al. Preparation and tribological properties of nanoparticle lanthanum borate. Wear 2000;243(1–2):43–7.
[36] Peng D-X, et al. Size effects of SiO_2 nanoparticles as oil additives on tribology of lubricant. Ind Lubric Tribol 2010;62(2):111–20.
[37] Goto M, Honda F. Film-thickness effect of Ag lubricant layer in the nano-region. Wear 2004;256(11–12):1062–71.
[38] Radice S, Mischler S. Effect of electrochemical and mechanical parameters on the lubrication behaviour of Al_2O_3 nanoparticles in aqueous suspensions. Wear 2006;261(9):1032–41.
[39] Bartz WJ. Some investigations on the influence of particle size on the lubricating effectiveness of molybdenum disulfide. A S L E Transactions 1972;15(3):207–15.
[40] Qiu S, et al. Preparation of Ni nanoparticles and evaluation of their tribological performance as potential additives in oils. J Tribol 2001;123(3):441–3.
[41] Mizuhara K, Tomimoto M, Yamamoto T. Effect of particles on lubricated friction. Tribol Trans 2000;43(1):51–6.
[42] Liu W, et al. The research and application of colloids as lubricants. J Dispersion Sci Technol 2000;21(4):469–90.
[43] Cizaire L, et al. Mechanisms of ultra-low friction by hollow inorganic fullerene-like MoS2 nanoparticles. Surf Coating Technol 2002;160(2):282–7.
[44] Li H, et al. Polysulfone/SiO2 hybrid shell microcapsules Synthesized by the Combination of pickering Emulsification and the solvent evaporation Technique and their Application in self-lubricating composites. Langmuir 2017;33(49):14149–55.
[45] Kumar A, et al. Particle behavior in two-phased lubrication. Wear 1997;206(1–2):130–5.
[46] Jiao D, et al. The tribology properties of alumina/silica composite nanoparticles as lubricant additives. Appl Surf Sci 2011;257(13):5720–5.
[47] Tang Z, Li S. A review of recent developments of friction modifiers for liquid lubricants (2007–present). Curr Opin Solid State Mater Sci 2014;18(3):119–39.
[48] Gulzar M, et al. Dispersion stability and tribological characteristics of TiO2/SiO2 nanocomposite-enriched biobased lubricant. Tribol Trans 2017;60(4):670–80.
[49] Tang J, et al. Improved tribological performance of amorphous carbon (a-C) coating by ZrO2 nanoparticles. Materials 2016;9(10).
[50] Darminesh SP, et al. Recent development on biodegradable nanolubricant: a review. Int Commun Heat Mass Tran 2017;86:159–65.
[51] Kao MJ, Lin CR. Evaluating the role of spherical titanium oxide nanoparticles in reducing friction between two pieces of cast iron. J Alloy Comp 2009;483(1):456–9.
[52] Li B, et al. Tribochemistry and antiwear mechanism of organic–inorganic nanoparticles as lubricant additives. Tribol Lett 2006;22(1):79–84.