Formulation of polymer-based lubricant for metal forming

G Ngaile[1]*, J Cochran[1], and **D Stark[2]**

[1]Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina, USA

[2]Sisu Chemical, LLC, Raleigh, North Carolina, USA

Abstract: A new metal forming lubricant based on polymeric materials has been developed. The lubricant has been developed through emulsion copolymerization. Copolymers with the common composition of stearyl methacrylate and 2-hydroxyethyl methacrylate acid phosphate were made with three secondary polymers: methyl methacrylate, butyl acrylate, and 2-hydroxyethyl methacrylate. The performance of the developed lubricant was evaluated using the ring compression and twist compression tests. The performance of the polymeric lubricant was compared against a zinc-phosphate-coating-based lubricant, commonly used in forging, and three other commercial lubricants. The polymeric lubricant exhibited at least equal performance in all tests conducted at room temperature. Preliminary test results show that the developed lubricant can be used effectively for non-severe deformation processes such as cold heading and extrusion processes with low surface expansions.

Keywords: lubricant formulation, metal forming, environmentally friendly lubricants

1 INTRODUCTION

Metalworking lubricants can be classified into four groups: water based, oil based, synthetic, and solid film. The effectiveness of lubricants in metal forming depends on a multitude of variables pertaining to the process, the die–punch system, the deforming materials, and the lubricant. Process variables include interface pressure, sliding velocity, interface temperature, and surface expansion, whereas die and material variables consist of material characteristics, surface topographies, and hardness levels [1, 2]. The complex interrelationship of these variables inherent in a specific forming process calls for a lubricant with specific characteristics to achieve low friction at the tool–workpiece interface. The formulation of metalworking lubricants is also constrained by the need to minimize impact on the environment.

Lubricants for severe drawing operations usually contain additives such as chlorine, sulphur, and phosphorus. These additives are potentially hazardous and often require the use of volatile organic solvents for removal from formed surfaces [3–5]. In cold forging processes, a zinc-phosphate-coating-based lubrication system is widely used. The zinc phosphate is formed by chemical reaction of phosphoric acid and an iron matrix. Inspite of the fact that the zinc phosphate coating exhibits a high level of lubricity favourable for most cold forging processes, the lubrication system contains varieties of chemicals that make handling and disposal of waste hazardous. During the process, phosphating baths become polluted with heavy metals such as lead and cadmium [6–10]. The process also generates a sludge that contains base metals, heavy metals, oils, and other pollutants in both the bath and waste water. The majority of the bath and process water therefore cannot be recycled and must be treated as hazardous waste.

To minimize environmental impacts, efforts are continually being made to formulate new metalworking lubricants. Miller and Patel [11] used a polymeric ester to replace chlorinated additives, fatty acid soaps, and sulphurized materials in metalworking fluids. Recent studies show that boric acid

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*Corresponding author: Department of Mechanical and Aerospace Engineering, North Carolina State University, Campus Box 7910, Raleigh, NC 27695, USA. email: gracious_ngaile@ncsu.edu; gngaile@eos.ncsu.edu

can be used as a lubricant for metal forming processes. Boric acid (H_3BO_3) is a hydrate of boric oxide B_2O_3. When in contact with water, boric oxide will readily hydrate, converting to the lamellar solid boric acid. Its molecular structure, therefore, allows it to act as an effective solid lubricant [12]. The Environmental Protection Agency has categorized boric acid as benign and determined that the Clean Water Act does not consider it a pollutant [12]. Several researchers have shown that boric acid has a strong tendency to form a chemically bonded film on oxidized aluminium. This characteristic makes boric acid an effective lubricant for aluminium forging [13–15].

In developing environmentally benign lubrication systems, researchers have also been looking for best combinations between die coatings and billet lubricants [16, 17]. Klocke *et al.* [17] used a biodegradable rape-oil-based fluid (modified triglyceride) in combination with graded zirconium carbide (ZrC) physical vapour deposition (PVD) tool coating. This lubricant system has been shown to exhibit superior performance compared with chlorous mineral oil commonly used for drawing of stainless steel.

A literature review shows that little work has been done to formulate metal forming lubricants using acrylic and methacrylic monomers. These classes of emulsion polymers are commonly used for applications that result in direct skin contact or food contact and are generally considered safe.

The main objective of this study was to formulate a metal forming lubricant based on polymeric materials by emulsion polymerization, where the waterborne chemistry will incorporate the adhesion and stabilization mechanism within the matrix of the polymer. The emulsion copolymerization that was studied utilized stearyl methacrylate (a carboxylic acid functional monomer) and 2-hydroxyethyl methacrylate acid phosphate.

2 LUBRICANT FORMULATION

2.1 Lubrication mechanisms

One of the major quality requirements for a good bulk metal forming lubricant is that the lubricant should be able to follow the surface extension during deformation without breaking down, that is, the lubricant should adhere firmly to the surface of the deforming materials. The present study sought a lubricant film with three pseudolayers (I, II, III), each with different chemical/physical characteristics. As shown in Fig. 1, at the workpiece–lubricant interface the pseudolayer should exhibit higher adhesive strength to ensure the lubricant is bonded to the deforming material. On the other hand, the
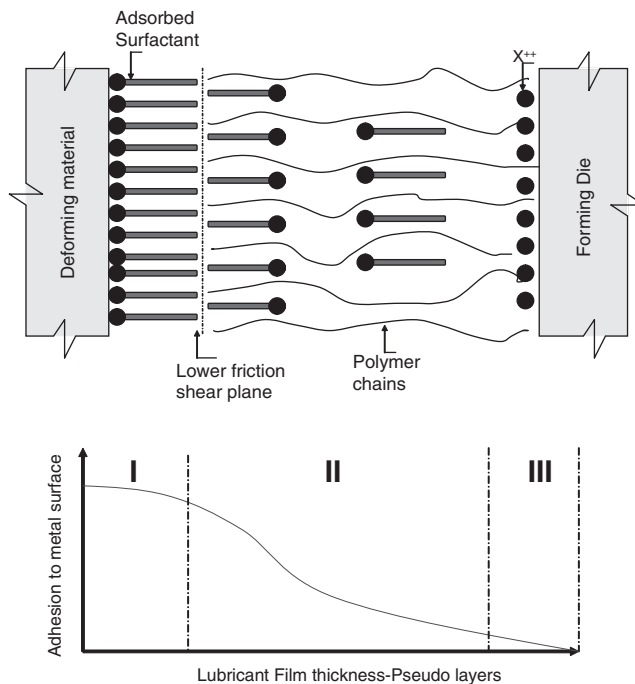

Fig. 1 Targeted physical and chemical characteristics of the lubricant film

lubricant film at the die–lubricant interface should have lower adhesive strength. The middle layer should exhibit low shear strength by virtue of arrangement of polymeric molecules. For this lubricant mechanism to occur, however, the die material should have less chemical affinity to the lubricant. If steel dies are used, the die surface should be coated so as to suppress chemical affinity of the polymer lubricant, that is, the adsorption of surfactant to the die side.

Another attribute of a good lubricant for metal forming is that it possesses self-repairing properties, that is, the ability of the molecules to reorganize themselves into the original state after being mechanically disrupted during deformation. Hsu [18] pointed out that the requirement for self-assembly would dictate that the molecules be free to move about on the surface. This implies that the molecules cannot be chemically bonded to the surface, hence the low bonding strength, which negates an important quality of the lubricant. Hsu [18] proposed that this dual problem be addressed by designing a lubricant that consists of molecules of the same functional group but with different chain lengths. Figure 2 shows a scheme for molecular design with long and short chains. The long chain is anticipated to behave like a liquid, and the short one like a solid. Similar function can be achieved by dispersing solid particulate in the polymer matrix as shown in Fig. 3. These approaches were used in the formulation of the polymeric lubricants discussed in this paper.
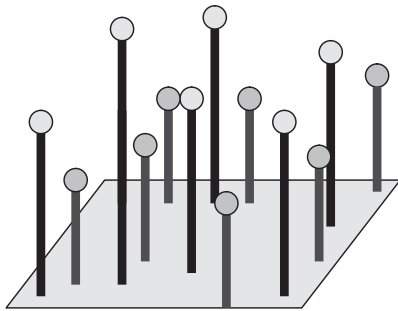
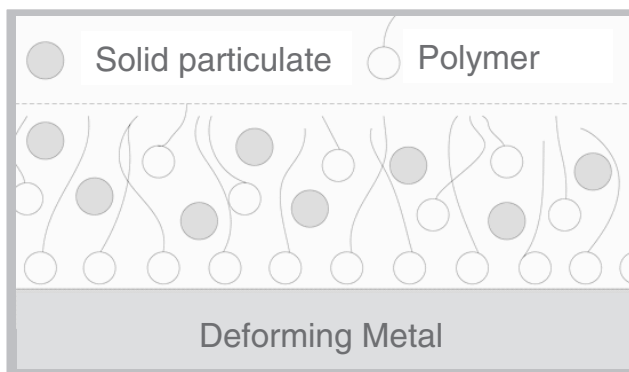**Fig. 2** Molecular design with different chain lengths, after Hsu [18]

Fig. 3 Targeted solid particulate dispersed in polymer matrix

2.2 Lubricant formulation through emulsion polymerization

The lubricant was produced by emulsion polymerization, where the water-borne chemistry incorporates the adhesion and stabilization mechanisms within the matrix of the polymer. The water-borne chemistry helps to wet out and adhere the lubricant directly to the surface of the metal with minimal pretreatment. Since water is the continuous phase, the products are characterized by low viscosity (providing ease of use) and high molecular weight (providing enhanced polymeric properties). Soaps are added to compartmentalize the organic and water phases and to form a stable emulsion. The wetting layer with this type of lubrication system includes the polymer combined with functionality that bonds with the metal surface. Thus, breaking of chemical bonds is required to remove the polymeric layer. The base polymer itself is a copolymer of monomers with long-chain aliphatic (fatty) pendant groups, providing the desired lubrication. The high molecular weight of the polymer generally improves properties such as heat resistance.

The emulsion polymerization employed in this study differs from the standard emulsion polymerization where soaps used to stabilize the polymers are associated to the polymer surface and not chemically bonded. When applied to a metal surface, the unbonded surfactants initially migrate to the interface, reducing interfacial surface energy and forming a soap layer on the surface. The polymer is then bonded to the surface by association to the surfactant in much the same way as the association for stability in the water phase. This, however, allows for the removal of the polymeric layer under high stress conditions. This is not a favourable condition for metal forming processes such as cold forging, where the interface stress can reach 3000 MPa.

In this study, various forms of lubricant were developed through copolymerization. Copolymers with the common composition of stearyl methacrylate (a carboxylic acid functional monomer) and 2-hydroxyethyl methacrylate acid phosphate were made with (a) methyl methacrylate, (b) butyl acrylate, and (c) 2-hydroxyethyl methacrylate.

Owing to the extreme hydrophobic nature of stearyl methacrylate (SMA), the incorporation of this monomer into an emulsion polymer poses difficulties. A known method of achieving high levels of SMA in an emulsion polymer is through mini- or microemulsion techniques, where the pre-emulsion is made with high levels of surfactant and then subjected to very high shear to reduce the particle size down to the order of magnitude of an emulsion polymer [19]. By this method, production scale is very equipment intensive, and no known mini-emulsion is made commercially. Once a polymer is achieved by this method on a lab scale, the emulsion must be sufficiently stable to prevent 'creaming' or separation of the polymer owing to the density differences between the polymer and the aqueous phase. Through surfactant iteration, the authors have developed the chemistry to manufacture high SMA containing polymers in standard emulsion polymer equipment, achieving a stable emulsion without the need for mini-emulsion techniques.

2.3 Polymeric lubricant variants

Various lubricant chemicals and physical properties were varied to obtain the best combination. The variables included molecular weight, different additives, and pH level. Table 1 shows the polymer variants used for emulsion polymerization.

Category I shown in Table 1 comprises methyl methacrylate/SMA copolymerization. The lubricant variants in this category were copolymers of methyl methacrylate, SMA, methacrylic acid, and 2-hydroxymethyl acid phosphate. Methyl methacrylate (MMA) was used because it provides a spacer molecule between the bulky SMA groups. MMA also gives a

Table 1 Polymer variants used for emulsion polymerization

Polymer group	Chemical structure	Basic structure
Category I		
Category II		
Category III		

non-branched linear polymer which improves the softening and flow properties upon heating.

Category II comprises butyl acrylate/SMA copolymerization. In this group of lubricant variants, the copolymers were made by substituting butyl acrylate for MMA to reduce the glass transition temperature, T_g. An increase in chain transfer agents also reduced molecular weight.

Category III comprises ethylhexyl acrylate/SMA copolymerization. This group of lubricant variants replaced butyl acrylate with 2-ethylhexl acrylate to further reduce the T_g. 2-Ethylhexyl acrylate (2EHA) has an eight-carbon branched pendant group that occupies a relatively high free volume around the polymer chain, allowing increased free rotation and reduced T_g.

3   EXPERIMENTAL SET-UP AND TEST PROCEDURES

Two tests were used to evaluate the lubricants: ring compression and twist compression. In a ring test, a billet with a hole drilled through the centre is compressed to various height reductions. The change in the inner diameter of the billet reflects the friction along the tool–workpiece interface. In low friction environments the inner diameter of the billet increases, and the opposite occurs under higher friction. In the twist compression test, a rotating annular tool is pressed against a fixed lubricated sheet metal

specimen at a predetermined pressure and sliding velocity. The torque transmitted to the sheet metal specimen is an indication of lubricant effectiveness.

3.1   Test setup

The ring compression test experimental setup is given in Fig. 4. The tooling for the ring test consists of two flat dies made of hardened A2 tool steel (RC 60). These dies are held in the tooling setup installed in a 150 t hydraulic press. The tooling has a capability for heating the dies up to 500 °C, and billets can be heated up to 1000 °C.

The experimental setup for the twist compression test is given in Fig. 5. The tools for this test are made from D2 tool steel material. The contact pressure between the tool and the sheet metal specimen is measured indirectly by multiplying the pressure measured in the hydraulic cylinder by the ratio between the cross-sectional areas of the cylinder and the annular tool. The pressure in the hydraulic cylinder is measured with a pressure transducer. The torque transmitted from the tool to the sheet metal specimen is measured with a torque transducer. Equation (1) is then used to calculate the coefficient of friction

$$\mu = \frac{T}{r_m PA} \qquad (1)$$

where μ is the friction coefficient, T is the applied torque, P is the applied pressure, A is the contact area and r_m is the mean radius of the punch.
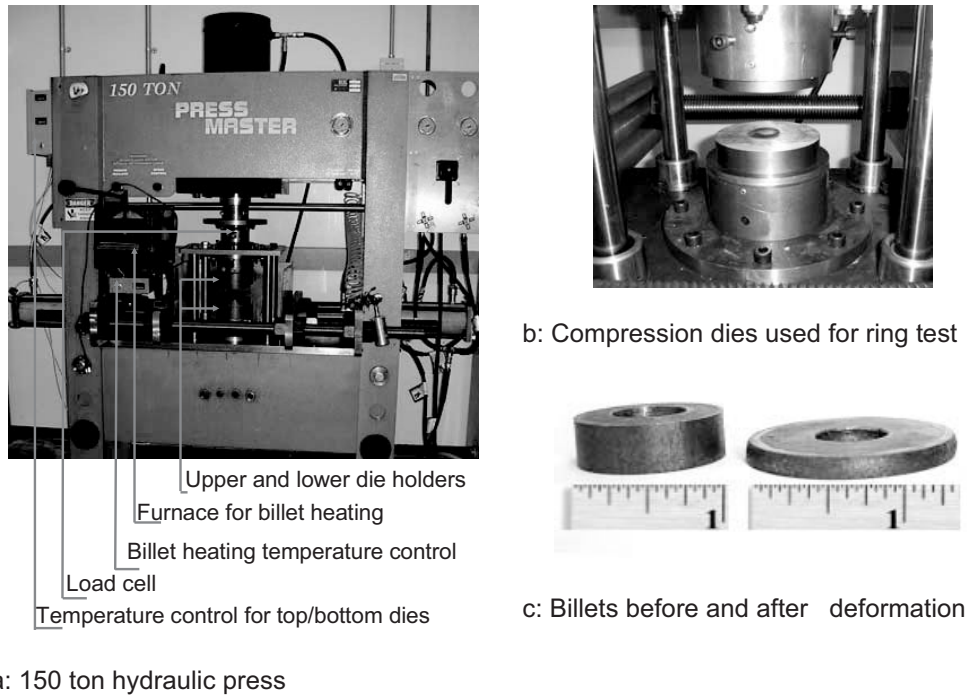
a: 150 ton hydraulic press

Upper and lower die holders
Furnace for billet heating
Billet heating temperature control
Load cell
Temperature control for top/bottom dies

b: Compression dies used for ring test

c: Billets before and after deformation

Fig. 4 Ring test experimental setup

Applied Pressure (P)

Applied torque

rm

Contact area (A)

Transmitted torque (T)

Die cross-section

19mm

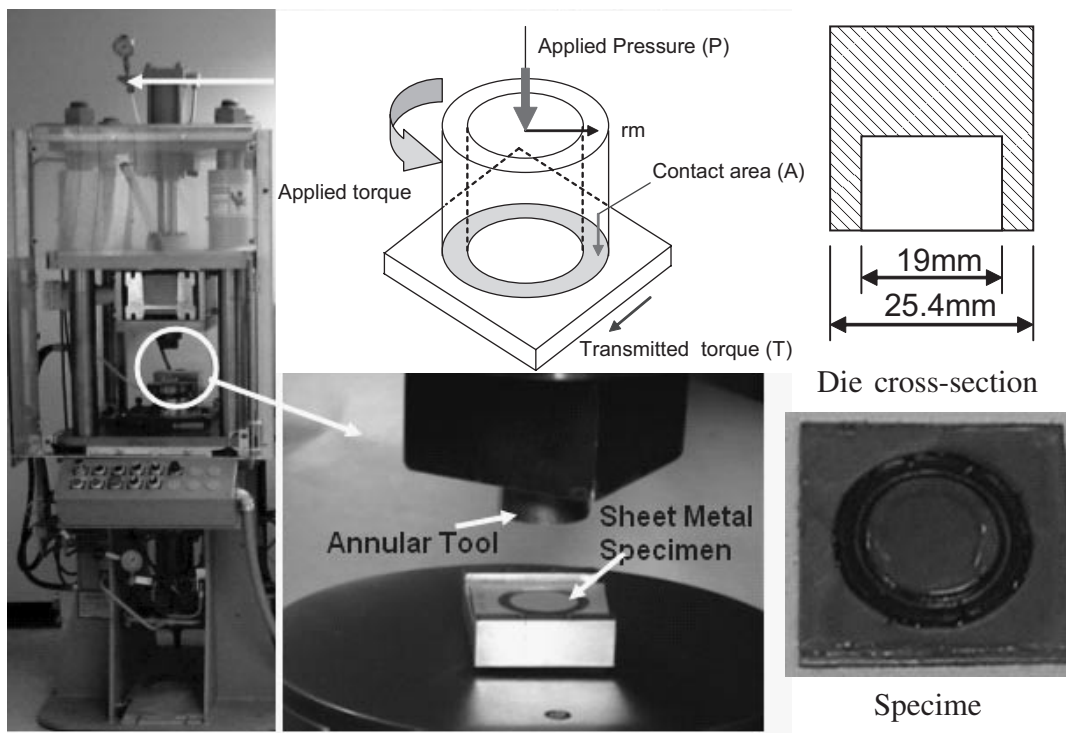25.4mm

Annular Tool

Sheet Metal Specimen

Specime

Fig. 5 Twist compression test experimental setup

3.2 Test procedures

The AISI 1018 samples were machined to 25.4 mm diameter by 8.4 mm height, with a 12.5 mm inner hole diameter at the centre of the sample. The samples were then dipped in the lubricant and dried at 40 °C before testing. After the deformed sample was removed from the press, the die surfaces were cleaned with acetone. The change in the inner diameter and the height dimensions during the test were computed and superimposed on the friction calibration chart to determine the friction level.

Nine samples were tested for each lubricant, that is, three samples for each reduction. The specimen height reduction levels were 20, 45, and 55 per cent. For the twist compression test the annular die was subjected to an interface pressure of 96 MPa and a rotational speed of 10 r/min. AISI 1010 steel and stainless steel (SS 304) specimens (50 mm × 50 mm × 2 mm) were used for this test.

4 RESULTS AND DISCUSSION

4.1 Performance of polymeric lubricant variants as a function of additive iterations using the ring compression test

4.1.1 Butyl acrylate/SMA copolymerization

Different additives were iterated to vary the lubricant chemistries as shown in Fig. 6. These additives included silicon emulsion and colloidal silicate. To facilitate self-repairing as discussed in section 2.1, copolymers with random chain lengths were used. When two different silicone emulsions were added to the lubricant base, a considerable drop in friction factor could be observed. When colloidal silicate was added to the lubricant base, no appreciable difference in lubricant performance was observed. The five lubricant variants resulted in a friction shear factor range $m = 0.13$–0.17.

4.1.2 Ethylhexyl acrylate/SMA copolymerization

Analogous to the butyl group, several additives were iterated as shown in Fig. 7. Hydrophilic surfactant was used to offset the extreme hydrophobic nature of the primary monomer, SMA. Hydrophobic describes the property by which the tail of the polymer will tend to be attracted to air and oil rather than to water. This is one of the challenges of producing stable emulsion (without phase separation) using SMA, as it is hydrophobic.

As can be observed in Fig. 7, the friction factor for the base copolymer was 0.13. An addition of 6 per cent silicon emulsion to the base copolymer lowered the friction level to $m = 0.12$. These friction levels were also improved by dipping the specimens in calcium nitrate prior to forming, which neutralizes the surface of the polymer, makes it bond less with the die, and lowers sliding resistance on the die surface. As seen in variant 5, calcium nitrate slightly reduced the friction level. In variants 4 and 5 a non-ionic surfactant was added to stabilize the emulsion over time.

The shelf life of the lubricant is an important consideration in lubricant development. A non-ionic surfactant was successfully used as a shelf-life enhancer. The influence of hydrophilic and hydrophobic surfactants was investigated. The hydrophobic surfactant has long-chain aliphatic groups on either end of the molecule, with a hydrophilic polar group in the middle. The hydrophilic surfactant has only one aliphatic group, with the polar group on the other end. Also, from variants formulated, hydrophilic surfactants exhibited better performance than did hydrophobic surfactants. The copolymerization from this group resulted in a friction drop from $m = 0.14$ to $m = 0.12$.

The usual pH value for most metalworking lubricants varies from seven to nine. In this study, acid was varied in order to determine how it influences
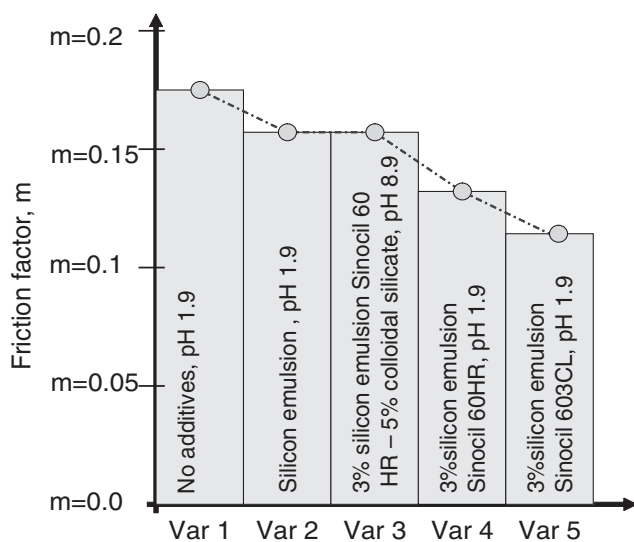

Fig. 6 Influence of butyl acrylate/SMA copolymerization on interface friction
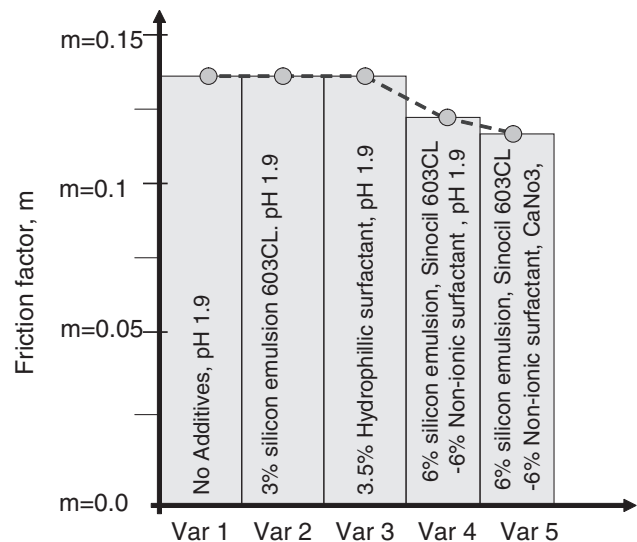

Fig. 7 Influence of ethylhexyl acrylate/SMA copolymerization on interface friction

the adhesion of the polymer to the surface. All the lubricant variants were later neutralized to pH 8, leaving only the ionized acid in the polymer for better mechanical stability. No significant difference was observed in performance.

4.2 Performance of the developed polymeric lubricants

4.2.1 Lubricant performance at room temperature

Five formulated polymeric lubricants were compared with three lubricants that are widely used in forging, extrusion, and drawing processes, as shown in Table 2. The criteria for selecting the five polymeric lubricants from over 20 formulated variants were:

(a) lower friction levels;
(b) higher shelf life/higher emulsion stability (2 months without phase separation);
(c) minimum stickiness characteristics for easy cleaning;

(d) higher wetting ability;
(e) strong adherence to the deforming metal.

Lubricant performance comparisons were carried out against four commercial lubricants:

(a) zinc phosphate coating + metal soap, a lubricant that is used in most medium and severe cold forging operations;
(b) MEC homat, a water-based lubricant used in non-severe forging operations;
(c) Lub BX, a solid lubricant used for non-severe cold forging;
(d) Lub CX, a solid lubricant used for drawing operations.

Figure 8 shows the performance comparison of Poly-Lubs 1, 2, and 3 against zinc phosphate coating + metal soap. Averaged experimental data points from the ring compression test are superimposed on friction calibration curves that were generated using finite element simulations. The curves show the friction factor, m, which quantifies

Table 2 Composition of the tested lubricants

| Lubricant	Composition	Remarks
Zinc phosphate	$Zn_3(PO_4)_2 + 6CH_3(CH_2)_xCOONa \rightarrow 3[CH_3(CH_2)_xCOO]_2Zn + 2Na_3PO_4$	Standard: zinc phosphate coating
Poly-Lub 1	Steryl methacrylate/butyl acrylate: 3% silicone emulsion, Sinocil 603CL-5% colloidal silicate, viscosity 12.56 cSt at 100 °F, pH 9.0	
Poly-Lub 2	Steryl methacrylate/2-ethylhexyl acrylate: 2% hydrophobic surfactant–6% silicon emulsion 603CL, viscosity 12.56 cSt at 100 °F, pH 1.9	
Poly-Lub 3	Steryl methacrylate/2-ethylhexyl acrylate: 2% hydrophobic surfactant–6% silicon emulsion 603CL, viscosity 12.56 cSt at 100 °F, pH 1.9	
Poly-Lub 4	Steryl methacrylate/methyl methacrylate; surfactant, pH 8.0	
Poly-Lub 5	Steryl methacrylate/methyl methacrylate; surfactant, pH 8.0	
Lub BX	Phosphoric compounds and solid lubricants	Not disclosed
Lub CX	Solid particulate in fluid	Not disclosed
Lub MEC	Water-based lubricant containing metal compounds and organic sulphur compounds. Commercially this lubricant is known as MEC homat produced by MEC International	
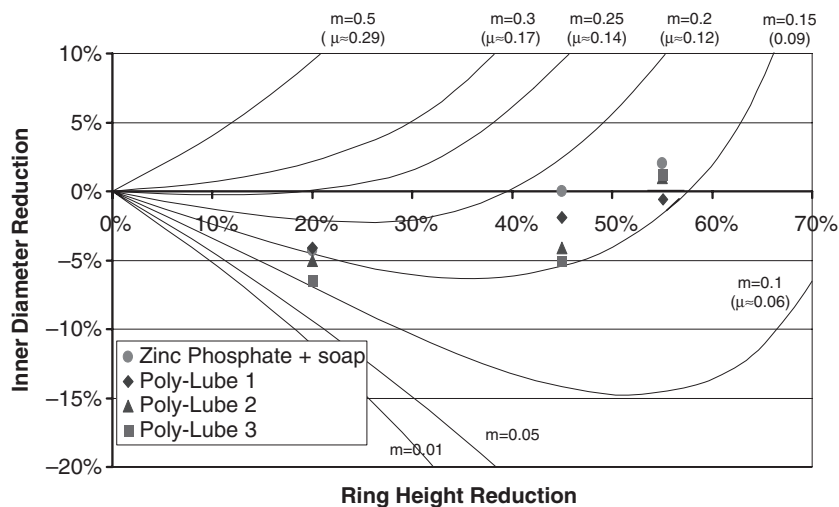
Fig. 8 Performance comparison between zinc phosphate and polymeric lubricants

lubricant effectiveness. The friction shear law was used, as it is more relevant for bulk metal forming than Coulomb's law. The friction shear law can be expressed as $\tau = (m\bar{\sigma})/\sqrt{3}$, $0 \leq m \leq 1$, where τ is the shear stress, m is the friction shear factor, and $\bar{\sigma}$ is the flow stress of the deforming material. The calibration curves also provide an approximation of the coefficient of friction, μ. Figure 8 shows that the polymeric lubricants consistently performed better than zinc phosphate at every level of reduction. When average friction values were taken for the three reductions, Poly-Lub 3 exhibited the lowest friction among the four lubricants tested, that is, $m = 0.15$ ($\mu \cong 0.087$). The average friction factor exhibited by the zinc phosphate coating + soap was $m = 0.175$ ($\mu \cong 0.1$). At higher reduction (55 per cent), however, Poly-Lub 1 exhibited the lowest friction.

Figure 9 shows a performance comparison of five polymeric lubricants against zinc phosphate. Poly-Lubs 4 and 5, which exhibit the lowest friction factor of the order of $m = 0.125$ ($\mu = 0.07$), were made from SMA/MMA. Surprisingly, after surfactant iterations, this polymer group (category I)

resulted in the highest lubricant shelf life of the three categories. The shelf life for category I was of the order of 5 months, while the other two categories exhibited observable phase separation within 60–90 days.

Poly-Lub 5 was also tested against commercial lubricant Lub CX, which is used for drawing processes. The results for the twist compression test are shown in Table 3. The lubricants were subjected to an interfacial pressure of 96 MPa on an AISI 1010 specimen. Poly-Lub 5 performed better than Lub CX. As seen in the Table, Poly-Lub 5 exhibited low initial peak friction and overall coefficient of friction of 0.051, whereas Lub CX exhibited a friction coefficient of 0.142.

Under the same condition as that used for steel specimens, the two lubricants were tested using SS 304 specimens. The twist compression results are given in Table 4. Again, Poly-Lub 5 performed better than Lub CX. As measured by the coefficient of friction, the lubricants performed similarly. However, Poly-Lub 5 had a longer time to breakdown, which suggests that Poly-Lub 5 develops greater film strength than Lub CX.
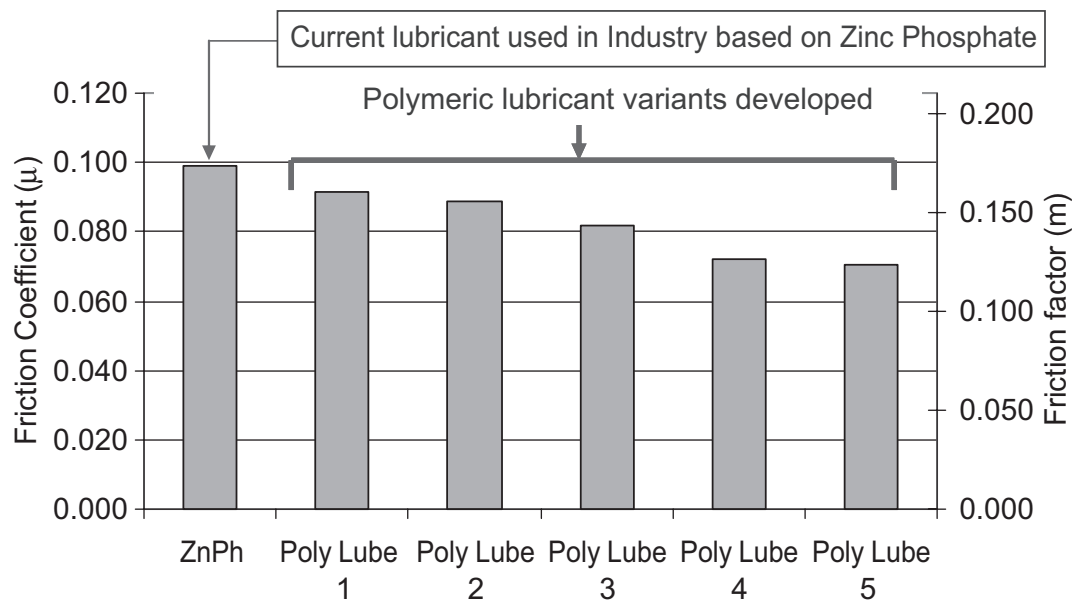

Fig. 9 Polymeric lubricant performance against zinc phosphate

Table 3 Twist compression test – steel specimens

	Initial peak		Friction coefficient		Time to breakdown (s)	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Poly-Lub 5	0.057	0.021	0.051	0.010	168	13.9
Lub CX	0.101	0.003	0.142	0.001	299	0

Table 4 Twist compression test – stainless steel specimens

	Initial peak		Friction coefficient		Time to breakdown (s)	
	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Poly-Lub 5	0.077	0.001	0.066	0.008	31.3	3.8
Lub CX	0.074	0.016	0.070	0.009	18.1	2.3
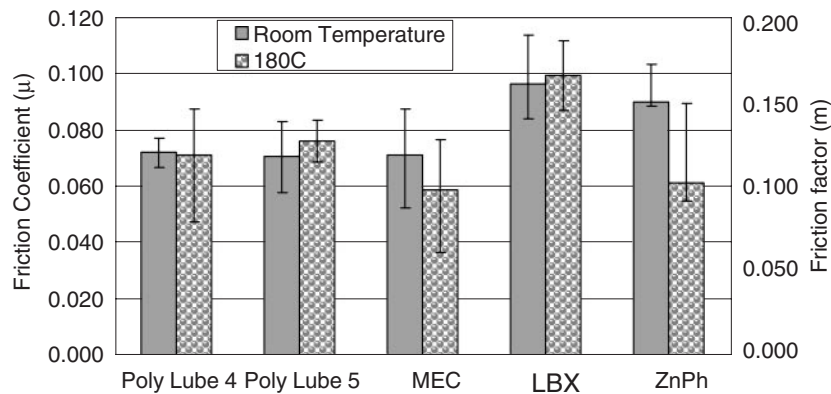
Fig. 10 Lubricant performance at elevated temperature

4.2.2 Lubricant performance at elevated temperature based on the ring compression test

One requirement for a good metal forming lubricant is the capacity to retain its lubricity at elevated temperatures. For example, the average temperature of the active tool surface in cold forging may typically be in the range 50–200 °C [20, 21]. Thus, in addition to testing lubricants at room temperature, the lubricants were also tested at elevated temperatures. Figure 10 shows that at elevated temperature there was no significant change in the performance of polymeric lubricants. ZnPh and MEC exhibited best performance, whereas LBX exhibited the worst performance.

5 CONCLUSIONS

Polymeric lubricants have been developed through emulsion copolymerization. Copolymers with the common composition of SMA and 2-hydroxyethyl methacrylate acid phosphate were made with three secondary polymers: MMA, butyl acrylate, and 2-hydroxyethyl methacrylate. The three classes of polymer lubricants, which in this study are distinguished by the secondary polymer used, were subjected to rigorous testing against commercial lubricants used for cold forging, extrusion, and drawing operations. The following conclusions are drawn from this study.

1. Under the ring compression tests, five variants of developed polymeric lubricants performed better than zinc phosphate coating + metal soap at room temperature. At elevated temperature, however, the zinc-phosphate-coating-based lubricant performed better than polymeric lubricants, that is, the performance of the zinc phosphate coating improved with increase in temperature, whereas the performance of polymeric lubricants did not show any significant change with increase in temperature.
2. Poly-Lub 4 and 5 performed equally to Lub MEC at room temperature, and both Lub 4 and Lub 5 performed better than Lub BX. Lub MEC and Lub BX are commercial lubricants used for non-severe forging operations.
3. Of the final five formulated polymeric lubricants, Poly-Lubs 4 and 5, which were made from the copolymerization of MMA/SMA, were found to have the longest shelf life.
4. Comparison performance carried out by the twist compression test showed that Poly-Lub 5 has superior lubricity to Lub CX.
5. The study demonstrated that Poly-Lub 4 and Poly-Lub 5 have the potential for practical applications, particularly for non-severe metal forming operations.

Although the lubricants formulated in this study are considered safe, their impact on the environment needs further investigation.

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