COMPLEXABLE POLYMERIC BINDER-LUBRICANT BLENDS

Y. Thomas, K. C. Cole and L. Tremblay*

Industrial Materials Institute/National Research Council Canada,
75 de Mortagne, Boucherville, Québec, Canada J4B 6Y4

** Quebec Metal Powders Limited,*
1655 Marie Victorin, Tracy, Québec, J3R 4R4

ABSTRACT

Lubricants are usually admixed into P/M mixes to primarily reduce die wall friction during compaction and make the ejection of the parts possible after compaction. However, conventional metallic stearates or EBS waxes lower the green strength of the parts. The P/M industry has sustained interest in developing new materials to improve the processability or the performance of P/M parts. An example of such a recent development is the use of new lubricant systems that increase the strength of the green parts.

This paper describes a new concept that can be used to enhance the green strength of the parts using complexable polymeric binders and lubricants. The ability of these systems to complex by the formation of strong intermolecular interactions is demonstrated using Fourier transform infrared (FTIR) spectroscopy.

1. INTRODUCTION

The production of compacted parts by powder metallurgy yielding high green strength is increasingly required, in particular for the manufacture of parts having a complex geometry or thin walls. High green strength enables parts to sustain the considerable stress that they experience when ejected from the compacting tool, minimizing the occurrence of cracks in the green body, as well as maintaining the integrity of parts during their handling between the compaction and sintering steps. With the advent of high performance materials that usually exhibit high apparent hardness and strength after sintering, high green strength also enables green machining prior to sintering, which helps to increase tool life, boosts productivity, and maintains competitiveness [1].

The mechanical strength of a compacted part depends on the level of mechanical and metallurgical cohesion between powder particles, and thus depends strongly on the powder compressibility. The main powder characteristics that affect the green strength, according to

Klar and Shafer [2], may be classified in three distinct groups related to geometric, intrinsic and surface factors. Indeed, a powder having an irregular shape or a high surface roughness will lead to higher mechanical interlocking between particles [3]. The presence of fine particles among the coarser particles also increases the green strength [4,5]. On the other hand, oxide layers at the surface of powders may inhibit cold welding and therefore limit the achievement of high green strength [6]. The presence of carbon or nitrogen in powders, reducing their ductility and therefore their compressibility, will also reduce the green strength. Warm pressing, however, by reducing the residual stresses in the metallic particles and thus increasing their ductility, can significantly increase the green strength of parts, usually enough to enable green machining.

In practice, metallurgical powder compositions contain alloying elements and organic additives, such as graphite, copper, nickel, lubricant and binder in order to optimize the flow of powders, the shaping process and the properties of final products. These additives generally reduce the mechanical strength of green compacts. Indeed, parts with significantly higher green strength are obtained from a non lubricated powder mix compacted with die wall lubrication, as compared to a powder mix containing conventional lubricants such as synthetic waxes or metallic stearates. This can be explained by the formation of a lubricating film with a low mechanical strength at the surface of the powder particles, which limits the microwelding during compaction [7,8].

The extent of the effect of the admixed lubricant on the green strength of the parts may however differ depending on the type of lubricant used and on its ability to enhance the powder compressibility. Indeed, over the last ten years efforts have been devoted to developing new lubricating systems. These are based either on composite waxes consisting of synthetic waxes, metallic stearates and other additives, or on polymeric lubricants. The development of new polymeric lubricating systems seems to be a very promising avenue to enhance the green strength of compacted parts, sufficiently high to enable machining prior to sintering [9]. However, more studies are necessary to better explore the feasibility of this avenue. Indeed, the compressibility and lubricating behavior of metal powder mixes containing polymeric lubricants could be significantly influenced by the type of polymers and the process conditions used (level of pressure, temperature and rate of compaction), which thus need to be taken into account in the choice of an adequate lubricant.

It is believed that the higher green strength observed when using polymeric lubricants is mainly due to their higher intrinsic mechanical properties compared with conventional lubricants. In particular, polymers differ from most conventional lubricants in that they are composed of macromolecular chains, which are built from numerous repeating fundamental units. However, it is worth mentioning that not all polymers exhibit adequate shear resistance as well as lubricating properties during compaction and ejection. As a function of their nature, structure and molecular weight, which is related to the length of the macromolecular chains, polymers may have different inherent mechanical and thermal properties (glass transition, softening and melting temperatures, etc.), which will greatly affect their shear resistances and lubricating properties under pressure for a given compacting temperature.

In particular, it is believed that the ability of some polymers to possess adequate lubricating properties may be related to the regular arrangement of the macromolecular chains and their ability to slide on one another when submitted to a shear force. Typically, polymeric lubricants used for dry pressing of metallic or ceramic powders include semi crystalline thermoplastic polymers such as polytetrafluoroethylene [10], polyolefins [11,12,13], polyethers like polyethylene glycol or poly(ethylene oxide)[14], polyesters [15,16,17] and polyamides [18,19].

Depending on the polymer properties and on the required characteristics of the metal powder mixes, the polymeric lubricant can be added as a powder, a coating by dissolution in a solvent or in the molten state. The advantage of polymeric lubricants is therefore that in some cases they can act both as a lubricant and a binder, for instance to reduce segregation and dusting of powder mixes.

This paper presents a concept that could be used to further improve the green strength of parts using complexable polymeric binders and lubricants. After describing the basis of this concept, some examples will present the green properties of an iron-based powder mix containing these new lubricating systems, as compared to a powder mix containing conventional ethylene bisstearamide (EBS) wax. The ability of these systems to complex by the formation of strong intermolecular interactions will then be demonstrated using Fourier transform infrared (FTIR) spectroscopy.

2. COMPLEXABLE POLYMERIC BINDER-LUBRICANT BLEND

Most polymers, except for saturated hydrocarbons such as polyethylene and polypropylene, contain functional groups that are either proton acceptors (basic groups) or proton donors (acidic groups). These functional groups enable these polymers to specifically interact with some solvents, plasticizers or other polymers but also with some substrates and reinforcing fillers, by acid-base and/or Van der Waals interactions. Hydrogen bonds are typical acid-base bonds. The strength of the hydrogen bonding between these proton donors and acceptors is a function of the acid or basic character of these functional groups [20].

When two polymers contain complementary donor and acceptor groups, they are able to establish specific intermolecular interactions by hydrogen bonding, and blends of these polymers are often miscible, which is not the case for most polymer blends. A wide variety of miscible blends with these characteristics are known. Those polymers contain either a proton donor (acid group) such as a hydroxyl, carboxyl, amine or amide group, or an electron donor group (basic group), such as amine group or oxygen atoms located on carbonyl, ether or hydroxyl group [21].

When the interactions between the donor and acceptor groups are particularly intense, blends of two polymers containing these complementary groups can form polymer-polymer complexes, also known as interpolymers. Most of these interpolymer complexes involve poly(carboxylic acid)s (or other polymers with a strong acid character like poly(4-vinyl phenol) or phenolic resin), together with polymers with a strong basic character. Such complexes are obtained, for example, when mixing poly (carboxylic acids) (like polyacrylic acid)) with poly(ethylene oxide), polyvinylpyrrolidone, poly(vinyl alcohol), polyvinyl-pyridine, or poly(ethyl oxazoline) [21,22,23].

It is noteworthy to mention that the interpolymer complexes possess unique properties, which are essentially different from those of the initial components [22]. Using a phenolic resin /

polyether blend, it was shown that depending on the ratio of the two polymers, more rigid thermoplastics or tougher thermosets with better mold release characteristics can be produced [24]. The complexation by hydrogen bonding between a phenolic resin and a polyether may be schematically visualized as shown in Figure 1.

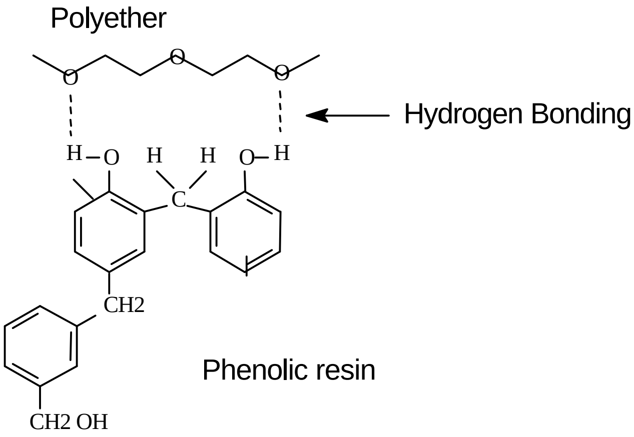

Figure 1 : Schematic Diagram Of The Polyether Molecule Fitting To A Polyphenol Molecule In Phenolic Resin [25].

The aim of this paper was to use this approach for powder metallurgy applications to further increase the green strength of parts compacted from mixes containing polymeric lubricants. This could be done by adding a suitable binder to the steel powder mixes that could interact with the polymeric lubricants by complexing acid-base interactions. While enabling the increase of green strength of the compacted parts, the binder should however have a limiting effect on the compressibility and lubricating performance during the compaction and ejection of the steel powder mixes.

This paper presents the effect of adding a polymeric binder having a strong acid character, such as phenolic resin, to a steel powder mix containing a polyether lubricant having a strong basic character, on both the processability and green strength of compacted parts. On the other hand, infrared characterization of the green parts was done to provide evidence that despite starting from solid polymeric and metallic powders, sufficient miscibility between polymeric binder and lubricant occurred during the processing of the powder mixes to enable the formation of interpolymer complexes.

3. APPLICATIONS : HIGH GREEN STRENGTH AND SOFT MAGNETIC PARTS

This section will present various results obtained with ferrous powder compositions containing specific polymeric binder-lubricant blends that can give rise to an interpolymer complex, by strong intermolecular acid-base interactions. Such compositions can be used for applications requiring very high green strength parts, such as green machining. Another application concerns the production of soft magnetic composites from mixes having enhanced processability and lubricating performance, while maintaining good mechanical properties.

3.1- High green strength parts using a polyether / phenolic resin lubricating system

The polymeric lubricating system comprises a polyether and a thermoset phenolic resin. Using conventional dry-mixing blenders, several powder mixtures were prepared containing 98.65 wt% ATOMET 1001 steel powder, 0.6 wt% graphite powder and different combinations of polyether and phenolic resin powders as described in Table 1. The polyether was a poly(ethylene oxide) having a weight-average molecular weight close to 100,000, while the phenolic resin was a resole-type phenolic resin.

Transverse rupture bars (3.175 x 1.270 x 0.635 cm) were compacted at a pressure of 45 tsi in a floating compaction die, and a temperature of 65°C to simulate frictional heat generated during typical production conditions. Ejection pressures were recorded for each mixture. A curing treatment for one hour at 175°C in air was done to cure the thermoset phenolic resin and improve the homogenization of polyether and phenolic resin. The green strengths were evaluated according to MPIF 15 Standard. Green and ejection properties of specimens containing either 0.75 % polyether or different combinations of polyether/phenolic resin were compared with those of a mix containing 0.75wt% ethylene bisstearamide EBS wax, as shown in Table 1. No curing was applied to the parts compacted with the EBS-containing mix.

Table 1 : Effect Of The Polymeric Lubricant / Binder Ratio On The Ejection And Green Properties

Polyether %	Phenolic resin %	EBS wax %	Ejection Pressure MPa (tsi)	Curing	Density g/cm³	Green Strength MPa (psi)
-	-	0.75	38.0 (2.75)	No	7.12	13.8 (2,004)
0.75	0	-	33.0 (2.4)	No	7.20	42.3 (6,134)
				Yes*	7.20	41.8 (6,057)
0.65	0.1	-	37.2 (2.7)	Yes*	7.18	71.7 (10,399)
0.45	0.3	-	41.3 (3.0)	Yes*	7.16	76.7 (11,127)
0.35	0.4	-	46.9 (3.4)	Yes*	7.14	83.0 (12,044)

* Curing in air at 175°C during one hour

It is seen that the use of a polyether lubricant in a steel powder mix significantly improves both the compressibility and the green strength of parts compared to the conventional EBS wax lubricant. On the other hand, while maintaining low ejection pressures and a good compressibility, the replacement of a part of the polyether lubricant by the phenolic resin enables the production of parts that have a much higher mechanical strength after curing than the parts containing either the polymeric lubricant alone or the conventional EBS wax. In particular, while providing similar ejection properties, the mix containing 0.65 wt% polyether and 0.1wt% phenolic resin had a green strength five times higher than the EBS containing mix. Still higher green strength was obtained when increasing the amount of phenolic resin up to 0.4%. However, in this case, a decrease of the lubricating performance was observed, with an increase of the maximum ejection pressure. The choice of the best formulation will thus be a compromise between the lubricating and mechanical properties required. It is believed that the high green strength obtained can be attributed to the ability of these polymers to flow between the metallic particles during the curing treatment and form a strong network, and to their ability to strongly interact via the formation of sufficiently strong intermolecular interactions that further strengthen the green compact, as will be shown later in this paper.

3.2- Soft magnetic iron/resin composites

AC soft magnetic composites can also be produced using the concept of complexable binder-lubricant blends. Indeed, for this application, the iron-based powder compositions contain an organic dielectric resin, which forms an insulating coating between the iron particles and also binds these particles so as to impart mechanical strength to the pressed parts. For instance, it has been shown that, using a phenolic resin as a binder, soft magnetic iron/resin composites with good mechanical and magnetic properties at frequencies up to 50-100 kHz could be obtained. If the mix does not contain lubricant, the compaction of parts requires the use of die wall lubrication. Conventional lubricants, such as zinc stearate and EBS wax, may be admixed to the mix to improve the processability of the iron/resin powder mix. However, they significantly decrease the strength of pressed parts. Thus, the use of a polyether lubricant in conjunction with the phenolic resin could be used to improve the processability of such soft magnetic composites, while maintaining good mechanical properties.

Using conventional dry-mixers, different powder mixtures were prepared containing ATOMET 1001 HP and different types and amounts of lubricants and phenolic resin powders. TRS bars were compacted at 65°C and 45 tsi in a floating compaction die and ejection pressures were determined. After a curing treatment (1h/175°C in air), the density and transverse rupture strengths were evaluated. Results are given in Tables 2 and 3.

Table 2 : Ejection And Green Properties Using Polyether/Phenolic Blend Versus Phenolic Resin

				Before curing		After curing	
Polyether %	Phenolic resin %	Die wall lubrication	Ejection Pressure tsi	Density g/cm³	Green Strength MPa (psi)	Density g/cm³	Green Strength MPa (psi)
0	0.8	No	4.6	7.14	22.0 (3,196)	7.14	112.5 (16,319)
0	0.8	Yes	2.4	7.17	-	7.16	121.4 (17,607)
0.4	0.4	No	2.9	7.27	37.7 (5,471)	7.27	97.7 (14,178)

Table 3 : Green Properties For Different Phenolic Resin / Lubricant Systems

Binder 0.6%wt	Lubricant 0.3%wt	Density g/cm³	Green Strength MPa (psi)
phenolic resin	PTFE	7.17	84.2 (12,220)
phenolic resin	Li-St	7.15	53.0 (7,700)
phenolic resin	polyether	7.20	102.6 (14,890)

Table 2 shows that, without the need for die-wall lubrication, the mix containing 0.4% phenolic resin/0.4% polyether enables at low ejection pressures to produce higher density parts than the mix containing only 0.8% phenolic resin, respectively 7.27 g/cm^3 vs 7.17 g/cm^3. On the other hand, even if the strength after curing is slightly reduced compared to a mix containing only phenolic resin, the mechanical strength of parts after curing with the polyether-phenolic resin blend is higher than the strength obtained with other lubricants (Table 3). Indeed, the measured strength value is twice that of the mix containing conventional lithium stearate lubricant, respectively 102.6 vs 53 MPa. Lower strength is also obtained with the PTFE/phenolic resin blend, for which no interpolymer interaction can occur. The lower deformability of the PTFE lubricant and its inability to flow between particles during the curing treatment may also partly explain the lower strength observed with this system. The use of a mix containing a polymeric lubricant and binder that are able to strongly interact by specific interpolymer interactions thus enables the production of soft magnetic parts with improved processability while maintaining good mechanical properties.

4. INFRARED CHARACTERIZATION OF THE COMPLEXING ACID-BASE INTERACTIONS

The object of this part was to demonstrate using Fourier transform infrared (FTIR) spectroscopy the ability of the polyether/phenolic resin system to complex by the formation of strong intermolecular interactions. IR spectroscopy, which is a well-known technique for both qualitative and quantitative characterization of materials, makes use of electromagnetic radiation in the mid-infrared range, typically from 4000 to 400 cm^{-1} (wavelength 2.5 to 25 µm). Absorption of the radiation occurs at certain specific wavelengths corresponding to the fundamental vibrational modes of the chemical groups constituting the molecules present in the material. As a result, it provides highly detailed information on the nature and concentration of the different chemical species present in the material.

Infrared spectra were measured on a Nicolet Magna 860 FT-IR spectrometer with DTGS detector in the 4000-400 cm^{-1} spectral region. The interactions between the polymeric binder and lubricant were first characterized by transmission on thin films of the pure polymers and on the polymeric blends (50/50). The system presented here concerns a polyether/phenolic resin blend. On the other hand, since the steel/lubricating system mixes are not transparent to radiation, it was not possible to characterize the complexing interactions for these mixes by the standard transmission IR technique. The “Praying Mantis” diffuse reflectance attachment (Harrick Scientific) was therefore used to collect diffuse reflectance infrared spectra. This was done on the fractured surface of cured TRS bars, compacted from mixes containing steel and

0.8% phenolic resin powders, and also from mixes containing steel and 0.4% polyether /0.4% phenolic resin powder blends (Figure 2).

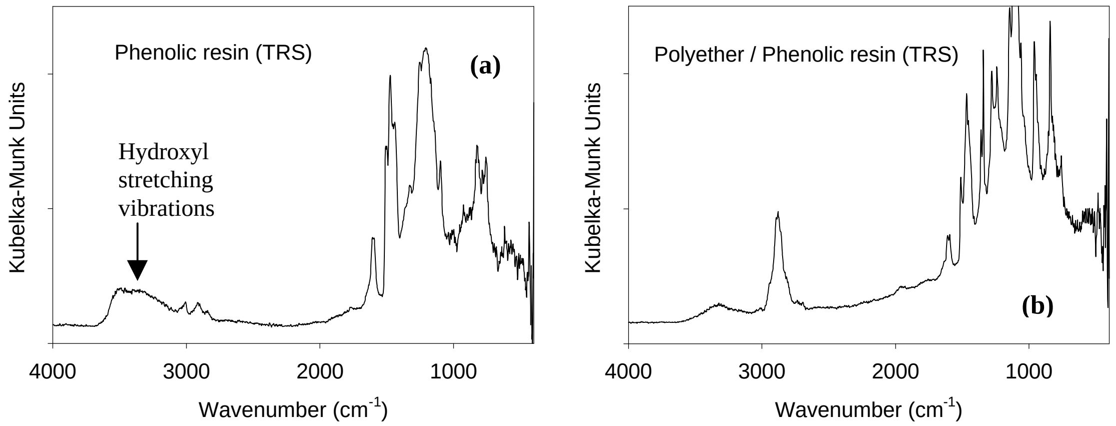

Figure 2 : Diffuse Reflectance Infrared Spectra Of The Fractured Surface Of Cured TRS Bars, Compacted From Steel Powder Mixes Containing (a) 0.8% Phenolic Resin, And (b) 0.4% Polyether / 0.4% Phenolic Resin

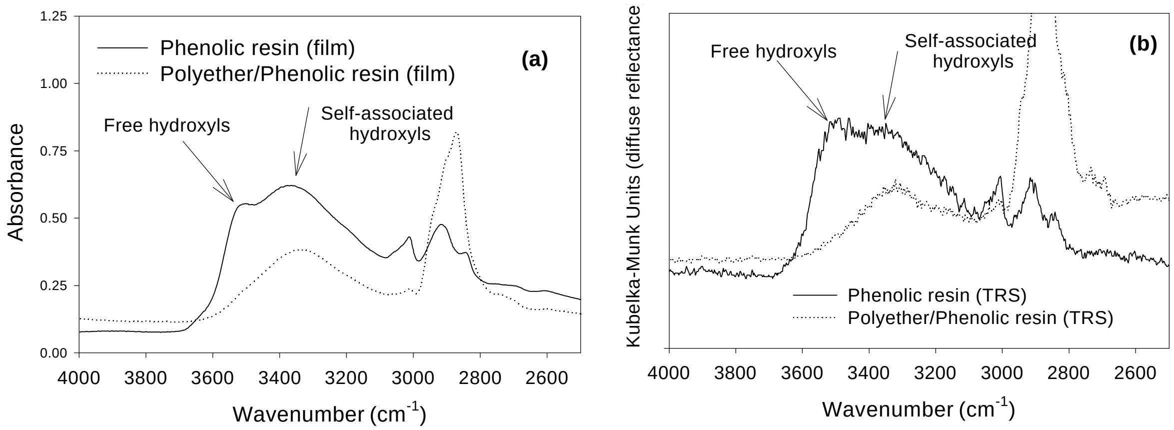

Figure 3 : Evidence Of Strong Hydrogen-Bonded Interactions Between The Polyether Lubricant And The Phenolic Resin Binder : (a) Film (Phenolic Resin Vs 50/50 Polyether/Phenolic), (b) Cured TRS Bars (0.8% Phenolic Resin vs 0.4%/0.4% Polyether/Phenolic, and 99.2% Iron Powder).

Figure 3 shows the corresponding hydroxyl stretching region, from 3700 to 3000 cm^{-1} for the phenolic resin and the polyether/phenolic resin blend either as cast films or on the fractured surface of TRS bars. The upper spectrum of pure phenolic resin shows an infrared band at 3500 cm^{-1} attributed to “free”or non-hydrogen-bonded hydroxyls and a broad band centered at 3365 cm^{-1} which is assigned to a wide distribution of hydrogen bonded hydroxyl groups (self-association of the hydroxyls groups of the phenolic resin) [26]. On the other hand, only one band centered at 3337 cm^{-1} is observed for the polyether / phenolic resin blend. Indeed, there is no evidence for the presence of free hydroxyls groups. This means that all the hydroxyl groups of the phenolic resin form hydrogen bonds with other hydroxyl groups of the phenolic resin (self-association) or with the ether oxygen groups of the polyether. Furthermore, the frequency shift from 3365 to 3337 cm^{-1} tends to indicate that the intermolecular interaction in the polyether-phenolic resin blend is stronger than the self-association of the hydroxyl groups in the phenolic resin itself.

The infrared characterization of the polymer films and the fractured surface of the TRS bars provides strong evidence of the formation of strong hydrogen bonds between the basic groups of the polyether and the acidic hydroxyl groups of the phenolic resin. As discussed previously, these strong acid-base interactions lead to the formation of interpolymer complexes that may explain the enhanced green strength of the compacted steel parts. It is noteworthy that despite the fact that the polymeric lubricant and the phenolic resin binder were only dry-mixed with the steel powders, similar interactions were seen on TRS bars, as compared to polymer films. This indicates that the conditions during the shaping process (compaction and heat treatment) are sufficient to enable a good miscibility of the two polymers and enable the formation of the interpolymer complex.

5. CONCLUSIONS

The recent development of new polymeric lubricants appears to be a promising avenue to enhance the green strength of compacted parts. This paper presented a concept that could be used to further improve the green strength of parts by adding suitable polymeric binders that are able to form interpolymer complexes with the polymeric lubricants. Indeed, with polymeric binder and lubricant that contain complementary acid and basic groups, it is possible to establish particularly intense intermolecular interactions by hydrogen bonding, and form interpolymer complexes.

Metallic powder mixes containing a polyether lubricant having a strong basic character, and a thermoset phenolic binder having a strong acid character significantly increased the green strength by a factor of six times after a curing treatment, as compared to conventional EBS. Such green strength should be sufficiently high to machine parts in the green state. Such compositions could also be used to produce soft magnetic composites having enhanced processability and lubricating performance, while maintaining good mechanical properties.

The improvement of green strength can be attributed both to the intrinsic properties of the polymeric binder and lubricant, which have the ability to flow between the metallic particles during the thermal treatment and form a strong network, together with their possibility to strongly interact via the formation of sufficiently strong intermolecular interactions that further strengthen the green compact. Evidence of strong hydrogen bonding between the phenolic binder and the polyether lubricant was shown on the green parts using Fourier transform infrared (FTIR) spectroscopy. Despite starting from solid polymeric and metallic powders, sufficient miscibility between polymeric binder and lubricant was shown to occur during the processing of the powder mixes and enable the formation of interpolymer complexes.

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