Study of bladder release agent formulas and methods to evaluate their efficiencies by using reciprocating tribometer

N Tanboriphan¹, B Teeraprawatekul², S Mahathanabodee³,⁴, and I Jangchud¹*

¹Department of Chemistry, School of Science, King Mongkut’s Institute of Technology Ladkrabang (KMITL), Bangkok 10520, Thailand
²Acme International (Thailand) Limited., Bangkok, 10250, Thailand
³Department of Production and Robotics Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok (KMUTNB), Bangkok 10800, Thailand
⁴Material Manufacturing and Surface Engineering Research Center (MaSE), Faculty of Engineering, King Mongkut's University of Technology North Bangkok (KMUTNB), Bangkok 10800, Thailand

*Corresponding author: ittipol.ja@kmitl.ac.th

Abstract. Bladder is one of the most important components in tire manufacturing process. In tire industry, methods to prolong bladder service-life and good bladder coatings for non-stick surface has been acquired. Bladder coated with good release agents can help reducing nonconforming products and increasing production efficiency. In this work, semi-permanent release agent formulas were studied. A new method to evaluate release agent efficiency by using a reciprocating tribometer were also carried out. Polydimethyl siloxane (PDMS) release agent formulas were developed with and without polymethyl hydrogen siloxane (PMHS). Effects of metal salt cure catalyst were also studied. In this work, method of release efficiency test was developed by using a reciprocating tribometer according to ASTM G133-05. It can be used to determine coefficient of friction of the coated surface and durability of the coatings. Coating durability test was also confirmed by repeating compression molding test to determine the number of release cycles. It was found that film durability was improved by adding the metal salt catalyst and PMHS. As the PMHS loading was increased, film endurance was improved to an optimum loading. Friction coefficient of the coatings could be related to the mold release ability and durability of the release agents. The technique can be used to estimate the service-life of the coated bladders. It can be used as a guideline for development of mold release agents in tire manufacturing industry.

1. Introduction
Release agents are chemicals used to prevent other materials from bonding to surfaces. They have been used in many industries such as medium density fiber board (MDF), fiber-reinforced composites, tire industry, etc. which require different release agents depending on their processes.
In tire manufacturing process, pneumatic tires are produced by molding and curing a green (or uncured) tire in a molding press. The green tire is pressed against a mold surface by means of an inner expandable “bladder”. Therefore, a release agent is needed to apply on the bladder surface in order to prevent adhesion between the bladder and inner liner of green tire in hot press of vulcanization process. For a semi-permanent release agent, its efficiency can be determined by numbers of cycles before re-applying the agent in the vulcanization process. Good bladder release agents can reduce nonconforming (NC) products, increase production speed, and extend bladder service-life.

In previous work [1-2], PDMS and PMHS were used as release agents. They provided excellent slippage yielding longer release ability [3]. The water-based release agent had a lower number of cycles carried out by the hot compression method. And the film endurance test was not carried out by the tribometer. In this work, the PDMS and PMHS have much better release ability and were evaluated both techniques. The objective of this work was to develop PDMS bladder release agents modified with PMHS. Effects of PMHS loading (0-6%) and addition of metal salt cure catalyst were studied. Another objective was to develop methods of release efficiency tests by using a reciprocating tribometer according to ASTM G133-05. It can be used to determine coefficient of friction and wear resistance of the coatings. Coating durability test was also confirmed by repeating compression molding test to determine the number of release cycles.

2. Experimental

2.1 Materials

Butyl rubber compound was purchased from Siamnavakam Co. Ltd., Thailand. PDMS, wax-based, and silicone-based release agents supported by Acme International Ltd., Thailand. PMHS and cure catalyst was purchased from Momentive Performance Materials Inc., USA. A wetting agent was obtained from BYK-Chemie Inc., Germany. Hexane was purchased from Koventure Co.Ltd., Thailand. All chemicals were used as received.

2.2 Sample preparation

Formulas of release agents are presented in Table 1. Some details of chemicals are kept proprietary. PDMS, PMHS, cure catalyst and wetting agent were mixed into hexane in 250 cm³ beaker. The mixtures were then stirred at 250 rpm for 1 min by using a mechanical stirrer (IKA RW20). After mixing, each sample was placed in a closed container.

| Chemicals   | Composition (% wt.) | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|-------------|---------------------|----------|----------|----------|----------|----------|
| PDMS        |                     | 5.54     | 5.54     | 5.54     | 5.54     | 5.54     |
| PMHS        |                     | 2.00     | 4.00     | 6.00     |          |          |
| Cure catalyst |                   | 0.50     | 0.50     | 0.50     | 0.50     | 0.50     |
| Wetting agent |                  | 0.20     | 0.20     | 0.20     | 0.20     | 0.20     |
| Hexane      |                     | 94.26    | 93.76    | 91.76    | 89.76    | 87.76    |

2.3 Specimens preparation

1 g of release agent sample was sprayed on 2.5 x 5 cm of the cured butyl rubber sheet (as a model for bladder). Then, the coated sheet rubber was placed into a hot air oven (Memmert UN55) at 150°C for 20 min to dry and cure the release agent film.

2.4 Physical and mechanical measurements

The friction coefficient and film endurance test were carried out by a tribometer [4] using a reciprocating mode according to ASTM G133-05 [5]. Each sample was tested at a load of 500 g against 6 mm tungsten
carbine ball. The test conditions were: 5 mm/s speed for 4 mm linear distance. Coating surfaces were examined under optical microscope (Olympus DSX1000).

Releasing ability of green tire and bladder was tested by repeating compression molding technique. Coated bladder samples were hot-pressed with green tire compound at a pressure of 2 MPa and temperature of 170⁰C for 5 min. Number of compression cycles was recorded until the surface of the specimens adhere to the green tire.

3. Results and discussion

It was observed that as the solvent appeared to substantially evaporate from the sample surface the release coatings appeared to dry to a glossy appearance.

3.1 Evaluation of surface coatings by tribometer

In the reciprocating mode in tribometer test, the sliding ball was moved on sample surface to monitor the frictional coefficient. Coating endurance can be determined from the transition of friction coefficient from stable to higher level [6]. It was found that the uncoated specimen (control) revealed high frictional coefficient of 1.1 due to rubbery surface of the substrate. As the samples were coated by release agents, frictional coefficient was decreased to the range of 0.25-0.30. By adding the metal salt catalyst (Sample 2 vs. Sample 1), film durability was improved. As the PMHS loading was increased, film endurance was increased. PMHS was converted into film to produce a resilient waterproof coating by using the metal salt catalyst at low temperature [7]. PMHS film shows good lubricating effect with outstanding water repellent property. Sample 1 had the least film endurance, whereas Sample 4 had the most film endurance as shown by the longest sliding distance.

![Graph showing coefficient of friction vs. Distance](image-url)
Figure 2. (a) Evaluation of friction coefficient vs. sliding distance on Sample 4 and corresponding optical micrographs showing wear tracks (b) at 20 m sliding distance and (c), (d) at 150 m sliding distance.

As shown in Figures 2a and 2b, a stable frictional coefficient of 0.25 at a distance of 0-62 m revealed existence of the release agent film. However, the coefficient of friction was raised to the value of 1.1 after 62 m meaning the tungsten carbide ball reached the rubber substrate as shown in Figures 2c and 2d.

3.2 Comparison of release agent efficiency

Figure 3. (a) coefficient of friction vs distance by tribometer (b) number of release cycles from repeating compression molding test and (c) coefficient of friction of each sample after failure.

In order to verify the release efficiency, comparative study of Sample 4 and other two commercial release agents (wax-based and silicone-based) were carried out. It was found that the commercial release agents had a higher coefficient of friction and lower stable distance value as shown in Figure 3a. The release efficiencies of each release agents were confirmed by repeating compression molding test. The number of release cycles by hot compression method of wax-based, silicone-based, and Sample 4 were 6, 9, and 37 cycles respectively [8] as shown in Figure 3b. Interestingly, it was found that the coefficient of friction on each sample after failure was in a range of 0.6-0.7 as shown in Figure 3c.
4. Conclusion
In this work, PDMS with PMHS release agent for bladder was developed. By adding the metal salt catalyst, film durability was improved. As the PMHS loading was increased, film endurance was increased. By using a reciprocating tribometer, friction coefficient of the release agent film was evaluated and tested for film durability. As confirmed by repeating compression molding test, efficiency of the release agents was estimated and used as a guideline for developing release agents in tire industry.

Acknowledgement
The research team is grateful to King Mongkut's Institute of Technology Ladkrabang (KMITL), King Mongkut's University of Technology North Bangkok (KMUTNB), and the National Science and Technology Development Agency (NSTDA) for co-financial supports. Thanks, are also to Acme International (Thailand) Ltd.

References
[1] H Brian 1994 U.S. patent no.0385919B1.
[2] F Louis 1982 U.S. patent USRE32318E.
[3] K Teerasurasassawat and P Koomsok 2018 Development of Mold Release Agent Formulas for Bladder in tire Industry., B.S. Thesis, KMITL, Thailand.
[4] W Gary 2006 International journal of adhesion and adhesives. 26 577-599.
[5] ASTM G 133-05. 2005. Standard test method for linearly reciprocating ball-on-flat sliding wear.
[6] G Biresaw and Mittal K.L 2008. Surfactants in tribology, CRC Press, 101 pages.
[7] http://www.silicone-surfactant.com/ Methyl-Hydrogen-Silicone-Fluid.htm: November 2021.
[8] S Mahathanabodee 2021. Effects of Mold Release Agent on Adhesion of Molding Materials., National Science and Technology Development Agency, KMUTNB, Thailand.