ADDING VALUE TO PVC FORMULATIONS WITH ESTER LUBRICANTS AND FINE CALCIUM CARBONATE

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Abstract

The PVC formulator is constantly challenged to improve performance while lowering cost. This paper reports on a laboratory project where three lubricant systems and three calcium carbonate products were evaluated.

A generic rigid PVC formulation, with 1phr TiO_2, containing paraffin wax and a one-micron ground calcium carbonate, was compared with formulations containing two different ester lube packages and a finer precipitated calcium carbonate. The ester lubricated, fine precipitated carbonate filled, compounds demonstrated improved impact performance, especially at the lower test temperatures.

Introduction

A PVC formulation is generally considered to be improved if it delivers the required mechanical properties and processing performance at a lower cost, or if it improves performance without any increase in overall formulation cost. Ingredient suppliers are constantly working on new products designed to bring added value to the formulation. The relationship between the many formulation ingredients and the formulation's overall performance is a complicated one. For a change to truly add value it can not be a trade-off where an improvement in one property is exchanged for the reduction of another.

The ability of fine, sub micron, calcium carbonate to contribute to impact performance has been reported previously (1-4) and has been in use commercially for over twenty years. There have also been reports that ester type lubricants can improve the value of a formulation when compared with the traditional lubrication system consisting of calcium stearate, paraffin wax, and PE wax. (5)

The experiment reported here is the first part of a project designed to explore the potential for PVC formulations that utilize a combination of both sub-micron calcium carbonate and ester lubricant systems.

Experimental

Table 1 contains the PVC formulations used for the experiment. There were five root formulations: 1) conventional, paraffin wax & calcium stearate, lube package with a one micron (average particle size) ground calcium carbonate 2) conventional lube package with a 1.2 micron precipitated calcium carbonate (top size equal to the 1 micron ground product) 3) conventional lube package with a 0.3 micron precipitated calcium carbonate (PCC). 4) fully esterified ester modified lube package with a CaStearate/paraffin blend and a 0.3 micron PCC 5) full ester lube package with HDPE lubricants and a 0.3 micron PCC.

Formulations 1 & 2 contain 4.5phr of impact modifier while formulations 3-5 contain 3.0phr of impact modifier. All formulations were run with calcium carbonate levels of 0, 10, 20, & 30phr.

The test blends were made by first producing 5 masterbatches without any calcium carbonate and then adding the calcium carbonate to produce the 19 different preblends.

The PVC preblends were melt compounded on a Banbury mixer, sheeted off on a two-roll-mill, cooled, granulated, and injection molded into 0.318 cm thick flex bars and impact disks on an Arburg injection molding machine. An in-the-mold transducer was used to adjust the injection pressure to maintain a constant cavity pressure for all samples. Izod test bars were cut from the molded flex bars and notched using a single tooth carbide cutter.

Notched Izod impact tests were run at room temperature (23 ^oC) on a Tinius Olsen Izod tester. An instrumented falling weight impact tester was used to test the disks. They were clamped onto a support with a 3.8 cm diameter center hole and impacted by a ½ in (1.27 cm) diameter tup, attached to a 59.0 kg weight, falling from a height of 20 cm. For the low temperature impact tests the test disks were preconditioned in a temperature chamber and removed from the chamber a few seconds before testing. Flexural modulus was measured with an Instron universal tester and three-point bending fixture.

Results and Discussion

The test results are reported in **Table 2** and displayed graphically in **Figures 1-4**.

Figure 1 – Notched Izod – The formulations containing the sub micron PCC with the conventional or ester modified lube packages produced the highest impact values. The ground carbonate and full ester formulations produced low values at the 10phr filler level, but substantially higher values at the 20 & 30phr filler loadings.

Figure 2 – Falling Weight Ductility at 23^{0}C – The ester lube formulations (4&5) were the only ones that produced 100% ductility at all three carbonate loading levels. The only conventional lube formulation that achieved 100% ductility was the one containing the sub micron PCC. This occurred at carbonate loadings of 20% & 30%.

Figure 3 – Falling Weight Ductility at 0^{0}C – All formulations were totally brittle at the 30phr carbonate loading level. All the conventional lube formulations were totally brittle, with the exception of the formulation containing 10phr of the sub-micron PCC. Both ester formulations demonstrated some ductility at the 10 & 20phr carbonate loading level. The only formulation that reached the 100% ductile level was the ester modified lube system with 10phr of the sub-micron PCC.

Figure 4 – Flexural Modulus - The reduction of impact modifier in formulations 3-5 produced an increase in stiffness. The highest modulus was achieved with the full ester lube formulation. All formulations produced a higher flex modulus than the conventional lube formulation containing the ground calcium carbonate. All formulations demonstrated a similar relationship between modulus and carbonate loading (slope of the curve) with the exception of the ester-modified formulation, which had a lesser slope.

The formulations containing the ester lube systems and 0.3 micron precipitated calcium carbonate produced the highest test results overall with dramatic improvements in falling weight ductility.

The next step in this project will be to measure the fusion characteristics of the compounds, adjust the lube levels if necessary, and run additional impact tests on extruded strip. We will also test a few selected compounds with even lower impact modifier levels.

Conclusion

The formulations containing the ester lubricants and 0.3 micron precipitated calcium carbonate out performed the other formulations. Formulation costs will vary depending on shipping charges and volume discounts. However, we estimate that the cost of these improved formulations will not be higher than the formulations with the conventional lube and filler. This makes the formulations with the ester lube and PCC the better value.

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References

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Keywords
PVC, Calcium Carbonate, Impact modifier, Impact properties, lubricant, ester

Table 1 – Experiment Design and Ingredient Levels (phr)

FORMULATION	1				2			3				4				5			
PVC Suspension Resin, K65	100				100			100				100				100			
Stabilizer, Alkyltin Mercaptide	1.25				1.25			1.25				1.25				1.25			
Calcium Stearate	1.0				1.0			1.0				0.5				1.0			
Paraffin Wax (165)	1.25				1.25			1.25				--				--			
Oxidized LD Polyethylene	0.15				0.15			0.15				--				--			
Acrylic Process Aid	1.0				1.0			1.0				0.5				0.5			
Fully Esterified Ester	--				--			--				0.9				1.2			
CaSt/Low Melt Paraffin 40/60	--				--			--				1.0				--			
Oxidized HDPE(low acid value)	--				--			--				--				0.1			
Oxidized HD Polyethylene	--				--			--				--				0.1			
Acrylic Impact Modifier	4.5				4.5			3.0				3.0				3.0			
Titanium Dioxide	1.0				1.0			1.0				1.0				1.0			
1 micron Ground Limestone*	0	A	B	C	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1.2 micron Precipitated $CaCO_3$*	--	--	--	--	A	B	C	--	--	--	--	--	--	--	--	--	--	--	--
0.3 micron Precipitated $CaCO_3$*	--	--	--	--	--	--	--	0	A	B	C	0	A	B	C	0	A	B	C

* A = 10phr, B=20phr, C=30phr

Precipitated Calcium Carbonate Products: TUFFGARD® (0.3µm), SUPER-PFLEX® MS (1.2 µm) supplied by Specialty Minerals Inc. Ground Calcium Carbonate product: CAMEL-CAL® ST supplied by Imerys. Ester lube products: Lubol® 352 (fully esterified ester), Lubol® GE-1 (calcium stearate/low melt paraffin), Lubol® 327 (oxidized, low acid value, HDPE) supplied by L&L Industrial Chemicals, Inc.

Table 2 – Test Results

	Notched Izod Impact Strength		Falling Weight (Dynatup) Ductility (%)		Flexural Modulus	
	ft-lbs/in	**J/m**	**At 23^0 C**	**At 0^0 C**	**Psi x 1000**	**Gpa**
1-0	**2.9**	**155**	**0**	**0**	**433**	**2.99**
1-A	**4.0**	**214**	**90**	**0**	**465**	**3.21**
1-B	**24.3**	**1297**	**30**	**0**	**506**	**3.49**
1-C	**22.3**	**1190**	**0**	**0**	**545**	**3.76**
2-A	**25.3**	**1350**	**80**	**0**	**477**	**3.29**
2-B	**26.7**	**1425**	**20**	**0**	**516**	**3.56**
2-C	**23.1**	**1233**	**0**	**0**	**547**	**3.77**
3-0	**2.5**	**133**	**10**	**0**	**454**	**3.13**
3-A	**27.1**	**1447**	**60**	**60**	**472**	**3.25**
3-B	**30.1**	**1607**	**100**	**0**	**513**	**3.54**
3-C	**30.0**	**1601**	**100**	**0**	**552**	**3.81**
4-0	**2.2**	**117**	**100**	**70**	**453**	**3.12**
4-A	**27.8**	**1484**	**100**	**100**	**477**	**3.29**
4-B	**30.9**	**1649**	**100**	**60**	**508**	**3.50**
4-C	**29.3**	**1564**	**100**	**0**	**546**	**3.76**
5-0	**2.0**	**107**	**100**	**30**	**453**	**3.12**
5-A	**8.5**	**454**	**100**	**90**	**482**	**3.32**
5-B	**29.4**	**1569**	**100**	**50**	**523**	**3.61**
5-C	**28.1**	**1500**	**100**	**0**	**567**	**3.91**

Figure 1

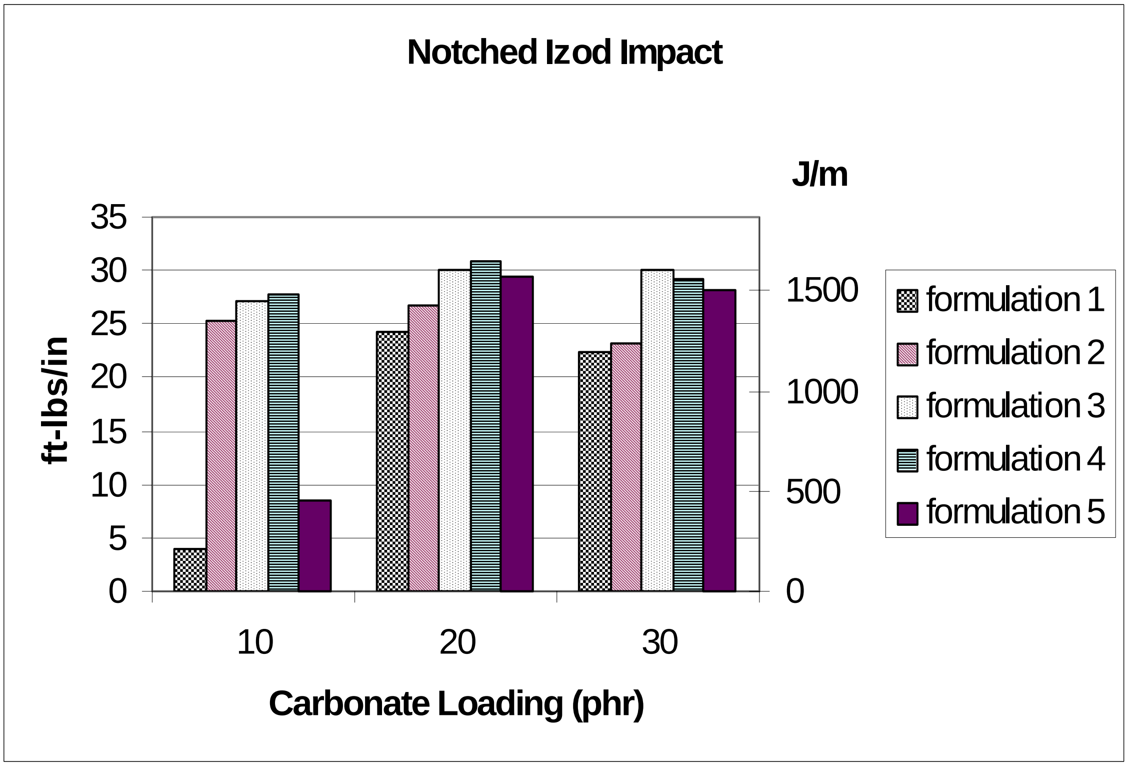

Figure 2

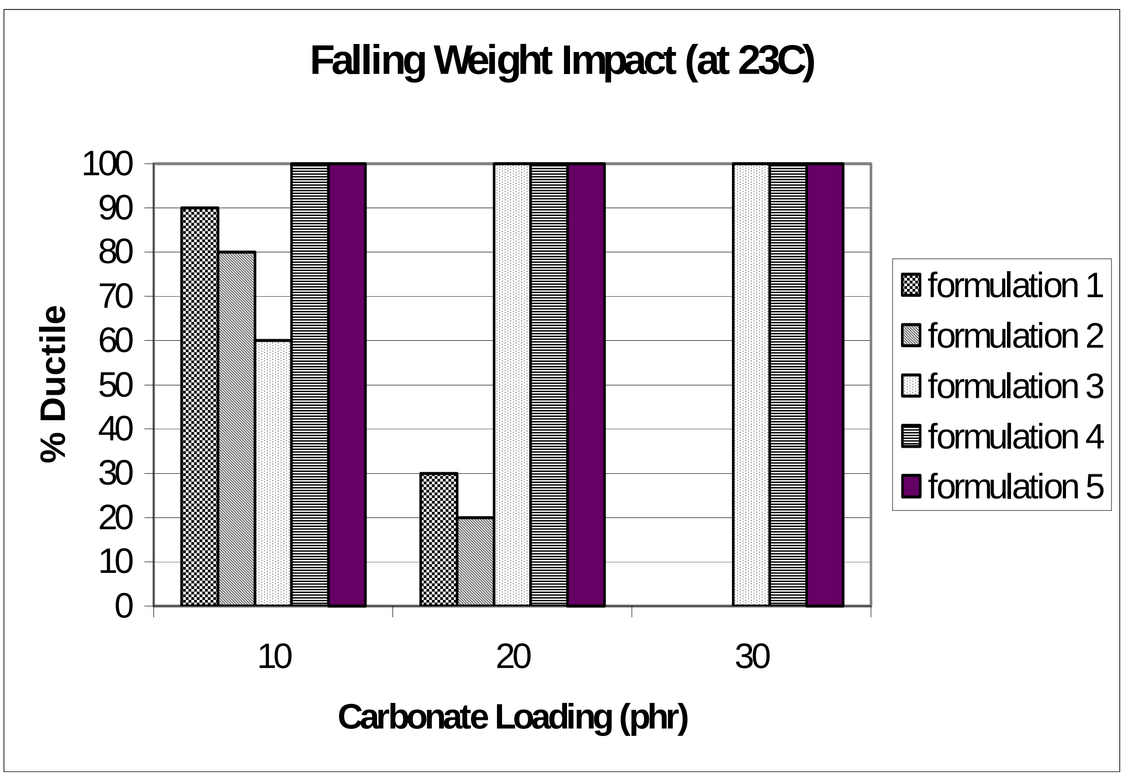

Figure 3

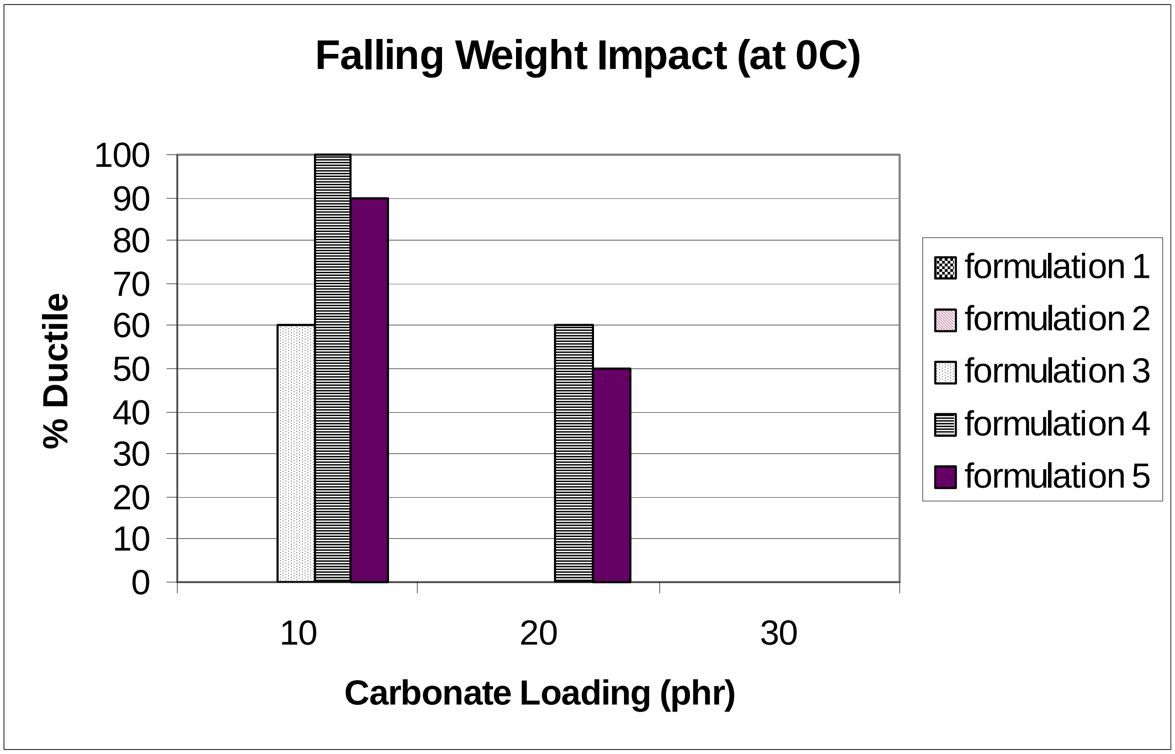

Figure 4