THE EFFECT OF CALCIUM CARBONATE SIZE AND LOADING LEVEL ON THE IMPACT PERFORMANCE OF RIGID PVC COMPOUNDS CONTAINING VARYING AMOUNTS OF ACRYLIC IMPACT MODIFIER

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Abstract

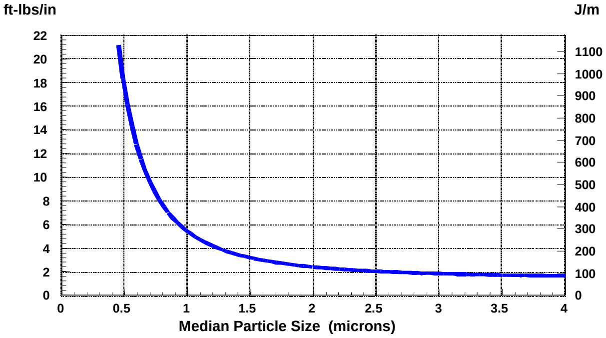
This study demonstrates how the impact performance of a rigid polyvinyl chloride (PVC) compound can be affected by the particle size of the calcium carbonate filler and its loading level. The test compounds contain 0 to 8phr of acrylic impact modifier and fillers ranging in size from 3 to 0.07 microns. By taking all three variables into consideration one can, not only optimize a compound's performance, but also lower its cost. Notched Izod and falling weight impact data will be reviewed. Flexural modulus and low temperature impact data are also included.

Introduction

PVC in its virgin form is virtually unusable from a mechanical property standpoint. Improvement of the mechanical properties of rigid PVC has been under investigation since its discovery in 1927. Because rigid PVC is brittle, additives are needed to increase its impact performance. There are two types of additives used to increase the impact performance of PVC: 1) polymer type impact modifiers (including acrylic, CPE and rubber-like materials), or 2) sub-micron (ultrafine) mineral fillers such as calcium carbonate. Factors that effect the impact performance are loading level of the additives and the mineral filler size. We acknowledge that processing conditions also affect the impact properties of the PVC, therefore every effort was made to keep all processing conditions constant for the experimental data presented in this paper.

The following graph illustrates the theoretical relationship between impact strength and particle size of calcium carbonate (1). As the particle size is decreased below 1 micron there is a significant increase in the impact strength of the material. Ultrafine calcium carbonates (and other minerals) do increase the impact performance of other polymers such as polypropylene (2), polyethylene (3-10), and polyketones (11). Experimental data has confirmed this relationship in our labs (12) and others (13) with PVC.

Notched Izod Impact Strength
20 phr calcium carbonate filled PVC



Coarse calcium carbonates have been used as inexpensive fillers and extenders. The use of ultrafine calcium carbonates as impact modifiers is not a new concept and has been practice for over 20 years (1). These fine products have been used in concert with acrylic impact modifiers or alone. A wide range of loading levels has been used depending on the application and desired mechanical properties.

The research reviewed here is intended to help PVC formulators minimize formulation costs. This will be apparent by illustrating the importance of selecting the appropriate calcium carbonate size and determining the appropriate loading level of filler and impact modifier. It will be shown that the formulator should let the calcium carbonate and impact modifier work together to maximize the impact performance of the PVC compound.

Experimental

Table 1 contains the PVC formulation used for the experiments. The fillers used had median particle sizes ranging between 0.07 to 3 microns and were either precipitated calcium carbonates (PCCs) or ground calcium carbonates (GCCs).[*]

Table 1. PVC formulation.

INGREDIENT	DESCRIPTION	LOADING LEVEL (phr)
Resin	Extrusion grade (K=66)	100
Stabilizer	dibutyltin bis	1.5
Process aid	Acrylic	1.0
calcium stearate	calcium stearate	0.5
Lube	fatty acid ester	0.8
Lube	High-molecular complex ester	0.5
impact modifier	Acrylic	0-8
Calcium carbonate	GCC and PCC	0-20

The test blends were made by first producing a masterbatch, without any impact modifier or filler, and then blending the remaining ingredients to produce the 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 °C) 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 diameter tip, attached to a 59.0 kg weight, falling from a height of 20 cm. The test disks were preconditioned in a temperature chamber and removed from the chamber a few seconds before testing. They were tested at 0, -10, and -20 °C. Flexural modulus was measured with an Instron universal tester and three-point bending fixture.

Results and Discussion

The results of the notched Izod impact tests are shown in graphic form (**Figures 1-4**) and in **Table 2** for several levels of impact modifier, carbonate loading level, and particle size. In general, the impact performance of the PVC was improved by increasing the concentration of the sub-micron calcium carbonate and impact modifier loading levels. This data demonstrates that a formulation can be developed with a lower level of impact modifier if a suitably sized calcium carbonate is used. This allows the formulator to maintain the desired impact resistance and reduce the overall cost of the formulation.

Table 2. Notched Izod Impact - J/m (ft-lbs/in)

Filler		**Impact Modifier Level (phr)**			
Size (microns)	**phr**	**0**	**2**	**4**	**6**
0.07	**10**	134 (2.5)	224 (4.2)	1575 (29.5)	1671 (31.3)
	15	214 (4.0)	1543 (28.9)	1601 (30.0)	1639 (30.7)
	20	1505 (28.2)	1623 (30.4)	1660 (31.1)	1687 (31.6)
0.3	**10**	144 (2.7)	219 (4.1)	1639 (30.7)	1676 (31.4)
	15	219 (4.1)	1665 (31.2)	1676 (31.4)	1697 (31.8)
	20	1671 (31.3)	1681 (31.5)	1719 (32.2)	1644 (30.8)
0.7	**10**	144 (2.7)	181 (3.4)	272 (5.1)	1649 (30.9)
	15	176 (3.3)	208 (3.9)	1665 (31.2)	1665 (31.2)
	20	240 (4.5)	1639 (30.7)	1623 (30.4)	1676 (31.4)
2	**5**	101 (1.9)	117 (2.2)	139 (2.6)	171 (3.2)
	10	112 (2.1)	133 (2.5)	149 (2.8)	166 (3.1)
	15	117 (2.2)	133 (2.5)	160 (3.0)	171 (3.2)
3	**5**	80 (1.5)	91 (1.7)	96 (1.8)	117 (2.2)
	10	80 (1.5)	91 (1.7)	101 (1.9)	112 (2.1)
	15	80 (1.5)	85 (1.6)	101 (1.9)	112 (2.1)
unfilled		75 (1.4)	91 (1.7)	133 (2.5)	203 (3.8)

The flexural modulus (**Figure 5**, **Table 3**) increased as the filler loading level was increased. As the impact modifier level was increased the flexural modulus decreased. There was a 16% increase in the flexural modulus when the filler loading was increased from 0 to 20 phr and the impact modifier level was reduced from 6 phr to 0 phr.

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[*] PCCs used: Ultra-Pflex® (0.07 μm) = Ultrafine $CaCO_3$, Tuffgard™ (0.3 μm), Super-Pflex® 100 (0.7 μm). GCCs used: Superfil® (2.0 μm), Hi-Pflex® 100 (3.0 μm). All supplied by Specialty Minerals, Inc.

A response surface was shown in **Figure 6** (data in **Table 4**) which demonstrates the effect of filler and impact modifier loading level on the notched Izod impact strength of rigid PVC containing the 0.07 μm calcium carbonate filler. Using this surface a formulator can "tune" a formulation to give the desired impact strength by changing either the filler and/or impact modifier loading level. As stated above, as the impact modifier level and filler loading level increase so does the impact strength of the material.

Table 3. Flexural Modulus - GPa (psi x 1000)

Filler		**Impact Modifier Level (phr)**			
Size (microns)	**phr**	**0**	**2**	**4**	**6**
0.07	**10**	3.49 (506)	3.35 (486)	3.24 (470)	3.16 (458)
	15	3.57 (518)	3.42 (496)	3.30 (478)	3.15 (457)
	20	3.69 (535)	3.51 (509)	3.39 (491)	3.21 (466)
0.3	**10**	3.60 (522)	3.52 (510)	3.38 (491)	3.22 (467)
	15	3.73 (541)	3.59 (521)	3.43 (498)	3.27 (474)
	20	3.96 (575)	3.73 (541)	3.52 (511)	3.38 (490)
0.7	**10**	3.63 (526)	3.57 (518)	3.41 (495)	3.32 (481)
	15	3.78 (548)	3.56 (517)	3.50 (507)	3.36 (488)
	20	3.94 (572)	3.76 (545)	3.63 (526)	3.39 (492)
2	**5**	3.42 (496)	3.35 (486)	3.21 (466)	3.18 (461)
	10	3.57 (518)	3.47 (504)	3.32 (482)	3.29 (477)
	15	3.69 (535)	3.59 (520)	3.45 (500)	3.41 (495)
3	**5**	3.51 (509)	3.39 (491)	3.28 (476)	3.17 (460)
	10	3.65 (529)	3.53 (512)	3.39 (492)	3.27 (474)
	15	3.79 (549)	3.67 (532)	3.56 (517)	3.41 (494)
unfilled		3.45 (501)	3.33 (483)	3.18 (461)	3.10 (450)

Table 4. Notched Izod Impact – J/m (ft-lbs.in)

Ultrafine CaCO$_3$ Level (phr)	**Impact Modifier Level (phr)**				
	0	**2**	**4**	**6**	**8**
0	37 (0.7)	37 (0.7)	48 (0.9)	64 (1.2)	112 (2.1)
3	27 (0.5)	43 (0.8)	59 (1.1)	96 (1.8)	1062 (19.9)
6	37 (0.7)	64 (1.2)	96 (1.8)	128 (2.4)	1046 (19.6)
9	53 (1.0)	96 (1.8)	133 (2.5)	1137 (21.3)	1340 (25.1)
12	75 (1.4)	155 (2.9)	1185 (22.2)	1276 (23.9)	1356 (25.4)
15	123 (2.3)	1148 (21.5)	1276 (23.9)	1377 (25.8)	1431 (26.8)

Table 5. Falling Weight Impact - % ductile

Ultrafine CaCO$_3$ level (phr)	**T (^{o}C)**	**Impact Modifier Level (phr)**				
		0	**2**	**4**	**6**	**8**
0	0	0	10	30	90	100
3		0	40	60	100	100
6		0	80	70	100	100
9		20	90	70	100	100
12		50	90	70	100	100
15		80	100	100	100	100
0	-10	0	10	10	100	100
3		0	20	40	100	100
6		0	30	60	100	100
9		0	30	60	100	100
12		0	30	60	100	100
15		0	30	90	100	100
0	-20	0	0	10	70	100
3		0	10	20	80	100
6		0	20	30	90	100
9		0	20	30	90	90
12		0	20	30	90	90
15		0	30	30	100	90

The Falling Weight Impact data is presented in **Table 5** for several temperatures. At 0 ^{o}C the same impact performance at high levels of impact modifier and no ultrafine CaCO$_3$ filler can be achieved by greatly reducing the level of impact modifier and the addition of ultrafine calcium carbonate. For example, a 90% ductile behavior was observed at 6 phr of impact modifier and 0 phr of ultrafine $CaCO_3$ filler as well as 2 phr impact modifier and 12 phr ultrafine $CaCO_3$ filler. However, at -20 °C there was no discernable difference in ultrafine $CaCO_3$ filler loading level. Only the high loading levels of impact modifier contributed to the ductile behavior at this low temperature.

Based on the above discussion one can see that a formulator can achieve the desired mechanical properties and minimize cost by reducing the level of more expensive impact modifiers and the use of ultrafine fillers. To be successful the proper filler must be used at a loading level where it can produce the desired effect.

Conclusion

Calcium carbonate can perform two ways in rigid PVC formulations. It can be a filler/extender or an impact modifier depending on the particle size. A sub-micron calcium carbonate can be substituted as an impact modifier. If too coarse a filler is used it can detract from, rather than enhance, impact performance. Filler loading level also plays an important role. If the filler level is too low, or too high, impact performance will not be optimized.

By optimizing the filler size, filler loading level, and impact modifier level in a formulation the processor can achieve the best possible performance at the lowest possible cost.

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Keywords

PVC, Calcium Carbonate, Impact modifier, Impact properties

Figure 1.
Izod Impact - 0phr Modifier

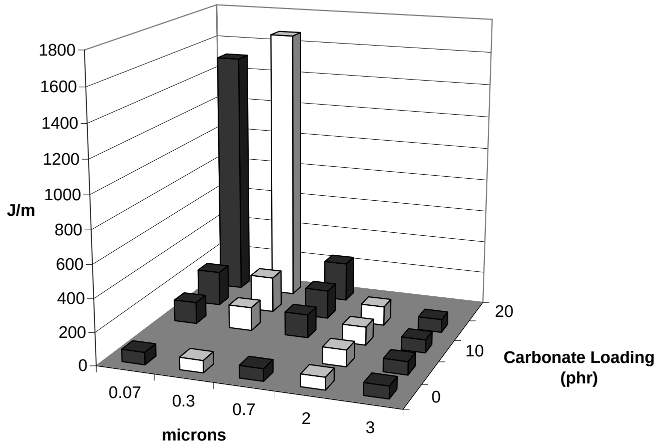

Figure 2.
Izod Impact - 2phr Modifier

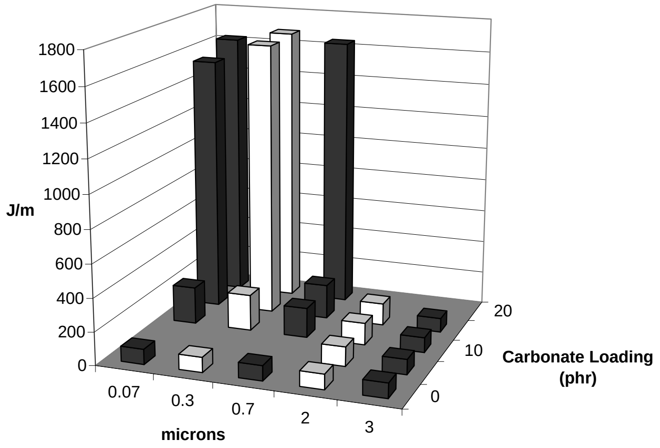

Figure 3.
Izod Impact - 4phr Modifier

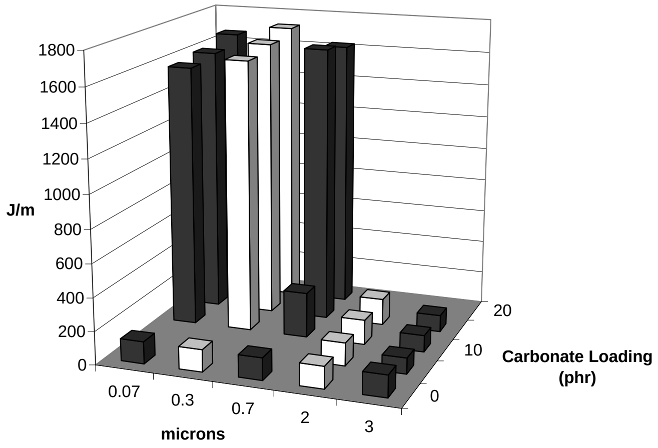

Figure 4.
Izod Impact - 6phr Modifier

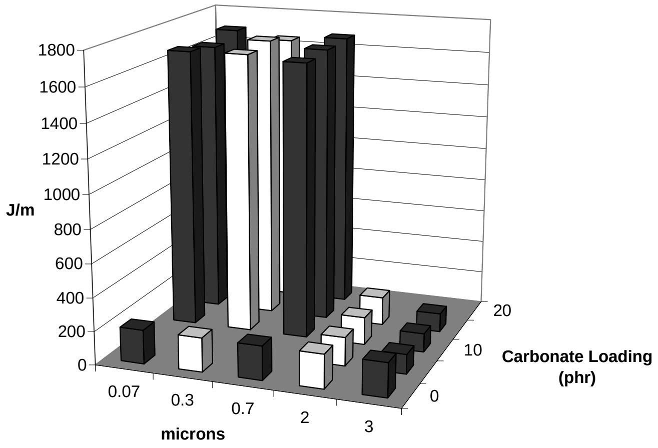

Figure 5.
Flexular Modulus (kPa x 1000)
0.07μm product

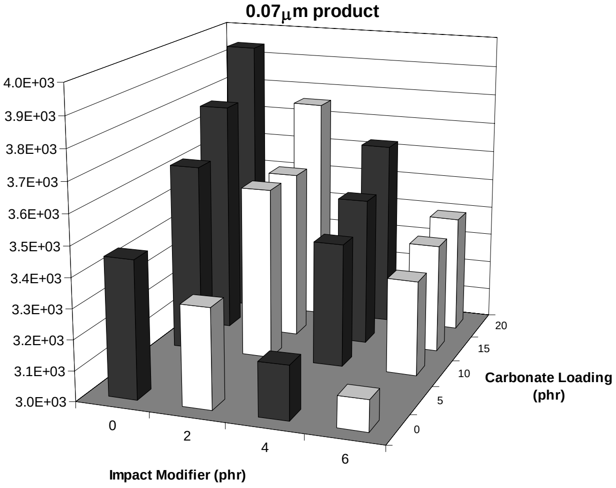

Figure 6.
Izod Impact
for 0.07 μm product