

## Improved Packaging Film Incorporating Vapor Phase Corrosion Inhibitors and High Recycle Content

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*Vapor phase corrosion inhibitors (VCIs) are used for safe and cost-effective protection of a wide range of metal articles. One large market includes packaging materials for storage and transportation of metal parts. Plastic packaging films can be readily impregnated with VCIs to provide corrosion protection, in addition to the basic physical barrier (against water, dirt, or vapors) afforded by the plastic. Generally, VCI-containing plastic films are recyclable. Likewise, they can be made from recycled plastics. However, when manufacturing with commercially available recycle streams, use of the recycled plastic is often limited by contamination and the extent of polymer degradation. This article discusses the benefits of using in-house recycling lines, including improved environmental profile, better quality, and cost savings. The results are supported by data and experience with in-house recycling lines at two production facilities.*

**Vapor phase corrosion inhibitors (VCIs)** are a well-known and highly versatile range of products for the prevention of corrosion.<sup>1</sup> VCIs can be delivered to the target metal

in a variety of ways. One common product is plastic packaging.<sup>2</sup> Plastic VCI films are a versatile and highly effective article for protection of items from corrosion. They are generally made from polyethylene (PE), which is readily available, cost effective, and usually recyclable.<sup>3</sup> Production of VCI films usually results in the production of at least some “scrap” film. This may be film of variable size produced during production start-up, or film that does not meet specifications. Scrap can be disposed of as trash, but is preferably recycled. The usual mode of recycling is to reprocess it (melt processing) into pellets that can be reused in production of new film.<sup>3</sup> It is often referred to as “repro.” Reprocessing can be done in-house with dedicated machines or the scrap can be sent to external facilities that specialize in recycling. The quality of repro can vary considerably with the quality/purity of the scrap and the conditions used for reprocessing (particularly temperature and shear).<sup>4</sup> In this article, studies are cited on varying the source and quantity of repro and the effects on product quality. Results and commercial implications are discussed.

### Experimental Procedures

#### Materials

##### PLASTIC RESINS

Commercial low-density PE (LDPE) and linear low-density PE (LLDPE) were used in proprietary combinations for the production of films. Slip and anti-block additives were used as necessary.

#### VCIs

VCIs were composed of proprietary formulations. The VCIs were added to the pellet blend as a master batch.

#### REPROCESSED PLASTIC RESINS

In-house reprocessed resin (repro) was prepared from VCI film scrap at two different facilities, using commercial re-granulator equipment. Some experiments utilized a commercial repro of LDPE. This was a clear material with a melt index of ~2 (2.16 kg, 190 °C). Sources varied.

#### Methods

##### MONOLAYER BLOWN FILM EXTRUSION

Films were produced on commercial blown film production lines in Cambridge, Minnesota, using standard melt processing temperatures in the range of 160 to 200 °C. Films contained a blend of commercial film-grade PE resins (LDPE and/or LLDPE). All samples contained a proprietary VCI, added as a master batch. Total concentration of active ingredients in the final film was ~2% by weight.

##### COEXTRUDED BLOWN FILM EXTRUSION

Films were produced on commercial blown film production lines in Beli Manastir, Croatia, using standard melt processing temperatures in the range of 160 to 200 °C. Films contained a blend of commercial film-grade PE resins (LDPE and/or LLDPE). All samples contained a proprietary VCI, added as a master batch. Total concentration of active ingre-

dients in the final film was ~1-2% by weight, depending on the specific film construction. The coextrusion die produced three layers (fed by three separate extruders). The general film construction included thickness/wt% of 25/50/25 for the three layers, respectively. VCI was added to one or more of the layers depending on the specific product.

#### PHYSICAL PROPERTY TESTING

The physical property testing was conducted with commercial testing instrumentation per the methods referenced below. These are primarily methods from ASTM for determining film thickness (caliper), ASTM D6988;<sup>5</sup> tensile properties, ASTM D882-02;<sup>6</sup> impact, ASTM D1709-04 Method A;<sup>7</sup> tear, ASTM D1922-06A;<sup>8</sup> coefficient of friction, ASTM D1894;<sup>9</sup> and seal strength, ASTM F88-99.<sup>10</sup> Puncture resistance was determined accord-

ing to Test Method 2065 of Military Standard 3010.<sup>11</sup> The results are generally shown with the number of digits in the instrument output report. However, for comparison purposes, differences between film sample results of less than about 10% are not considered significant. While the test methods can be quite precise, there is considerable variability in film samples due to small differences in composition and the effects of processing variables. In particular, physical properties of blown films are strongly dependent on orientation of the molecules in the film, which is a complex function of molecular structure, bulk melt viscosity/elasticity, processing temperatures, equipment design, cooling rate, processing speed, and blow up ratio (ratio of bubble diameter to die diameter).<sup>12</sup> Many material properties are measured in both the machine direction (MD) and transverse direction (TD), as these

properties are often different due to the different extent of orientation in these directions. For some properties, it is common for the MD and TD to be inversely correlated (as one increases, the other decreases).

#### VAPOR-INHIBITING ABILITY CORROSION INHIBITION TEST

The vapor-inhibiting ability (VIA) test measures the effectiveness of the VCI. Testing was performed by standard methods as previously described.<sup>13</sup> In brief, sanded carbon steel (CS) plugs are suspended from a modified lid in a quart jar. Strips of the test substrate, 1 by 6 in (25 by 150 mm) are hung from the inside of the lid, ensuring they do not come in contact with the plug. The jars are left to condition for 20 h at ambient temperature. After conditioning, a glycerol/water solution is added to the jars to accelerate cor-

**TABLE 1. COMPARATIVE DATA—MONOLAYER FILMS**

Property	Direction	Units	No Repr	15% Blue Repr	20% Blue Repr	15% Blue Repr, 5% Clear	10% Blue Repr, 10% Clear
Caliper	—	µm	107.95	105.92	106.17	107.70	106.17
Breaking Factor	MD	kN/m	3.43	3.13	3.05	3.02	2.95
	TD		3.29	2.77	2.88	2.80	2.79
Tensile Strength at Break	MD	MPa	32.96	30.08	29.89	28.66	27.75
	TD		31.19	27.15	28.19	26.83	26.26
Elongation at Break	MD	%	739.54	655.21	720.65	645.45	663.60
	TD		833.85	734.19	833.80	761.28	777.69
Yield Strength	MD	MPa	15.17	9.28	9.49	9.77	8.89
	TD		14.21	9.98	10.47	10.18	10.43
Dart Drop Impact Resistance	—	Grams	623.30	728.06	737.94	693.03	687.47
Puncture Resistance	—	N	32.52	32.29	34.03	29.98	32.61
Tear Strength	MD	mN	6,621.69	5,570.38	4,848.58	4,958.42	4,252.32
	TD		16,632.67	14,906.64	15,691.20	15,659.82	14,969.40
Coefficient of Friction	—	Static	0.20	0.52	0.49	0.55	0.50
	—	Kinetic	0.27	0.53	0.51	0.56	0.51
Seal Strength	—	kN/m	NA	1.70	1.64	1.60	1.60
Razor Blade (Steel)	—	—	Pass	Pass	Pass	Pass	Pass
Razor Blade (Copper)	—	—	Pass	Pass	Pass	Pass	Pass
VIA	—	—	Pass 3, 2, 3	Pass 2, 2, 2	Pass 2, 2, 3	Pass 2, 3, 3	Pass 2, 2, 3

**TABLE 2. COMPARATIVE DATA—MONOLAYER FILMS**

Property	Direction	Units	20% Blue Repro	15% Blue Repro, 5% Clear	15% Blue Repro
Caliper	—	µm	103.63	104.17	102.92
Breaking Factor	MD	kN/m	2.70	2.83	2.91
	TD		2.94	2.73	2.67
Tensile Strength at Break	MD	MPa	26.72	27.98	28.47
	TD		29.10	27.13	26.37
Elongation at Break	MD	%	622.70	715.11	737.55
	TD		733.96	792.60	773.75
Yield Strength	MD	MPa	9.05	9.40	9.30
	TD		10.37	10.14	9.98
Dart Drop Impact Resistance	—	Grams	742.03	719.53	701.20
Puncture Resistance	—	N	30.96	30.83	31.09
Tear Strength	MD	mN	6,966.89	64,96.16	6,904.13
	TD		15,377.38	15,377.38	15,942.26
Seal Strength	Left	kN/m	1.78	1.69	1.50
	Center		1.33	1.37	1.34
	Right		1.75	1.77	1.64

**TABLE 3. COEXTRUDED FILMS**

Property	Direction	Units	No Repro	40% Repro (Mid Layer) In House	40% Repro (Mid Layer), 30% In House, 10% Commercial
Caliper	—	µm	100	100	100
Breaking Factor	MD	N	61.68	60.61	55.07
	TD		60.93	65.67	56.05
Tensile Strength at Break	MD	MPa	22.72	21.92	22.00
	TD		24.63	24.02	22.50
Elongation at Break	MD	%	674.40	694.10	687.40
	TD		796.40	878.40	806.20
Tear Strength	MD	mN	6,696.96	8,580.48	6,121.44
	CD		21,346.56	17,893.44	15,382.08
Impact Puncture	—	N	17,605.68	17,684.16	16,428.48
	—	J	1.51	1.52	1.42
Coefficient of Friction	Kinetic	—	0.20	0.21	0.21
	Static	—	0.22	0.23	0.23

rosion and left to sit at ambient temperature for 2 h, then in a 40 °C oven for 2 h. The plugs are removed and rated on a scale of 0 (heavily corroded) to 3 (no visible corrosion). A grade of 2 or 3 is considered passing.

### RAZOR BLADE CORROSION INHIBITION TEST

This test measures the effectiveness of the film in preventing corrosion when in direct contact with a metal surface. Testing was performed by standard methods as previously

described.<sup>13</sup> In brief, CS panels are cleaned in methanol and dried. Two drops of deionized (DI) water are placed on the metal panel and covered with the substrate of interest. After 2 h, the substrate is removed and the panels are inspected. Panels with any sign of corrosion, pitting, or staining are deemed to “fail” the test. A second test is conducted with copper panels. The method is the same except that a 0.005% (by weight) sodium chloride (NaCl) solution is used instead of water and the test time is extended to 4 h.

## Results

### Monolayer Films

The films compared in Table 1 were produced on a machine with an 8-in (200-mm) diameter die, with a blow up ratio of 2:1. The “blue repro” is material made in-house from VCI scrap. The “clear repro” is commercially purchased material containing no VCI. The table shows a comparison of films containing up to 20% repro (in various combinations) with a comparable formulation containing all virgin resins (no repro).

All of the samples passed the corrosion inhibitor tests. Most of the physical property results are not considered to be significantly different. The differences in the coefficient of friction values are due to different levels of slip and anti-block additives in the formulations (not to the use of repro). There are possibly real differences between samples for yield strength, tear strength, and tensile strength at break, with the repro containing formulations showing slightly reduced properties. However, all films are perfectly acceptable for use.

There were no significant physical property differences between the samples using in-house (blue) repro and those using commercial (clear) repro. However, the samples made with the commercial repro had a large number of “unmelts.” These are physical defects in the film due to small pieces of plastic (~10 to 100 µm) that are visible in the film and create a rough feel to the surface. Unmelts may be caused by contamination in the resin, often from higher melting plastic contaminants in the reprocessing feed stream.

Table 2 shows results for a similar experiment run on a larger film line, with a die 20 in (500 mm) in diameter. The table compares films with 15 to 20% repro, in various combinations. Again, there were no significant differences between the physical properties at 15% or 20% repro, or with in-house vs. commercial repro. Again, however, the film made with commercial repro showed a large number of unmelts.

### Coextruded Films

The films compared in Table 3 were produced on a machine with a 400-mm diameter die, with a blow up ratio of 2:1. The repro is used at 40% in the center layer, which makes up 50% of the film structure, so the repro makes up 20% of the bulk film composition. Here again, the differences between physical properties of the films are mostly not significant, with the possible exception

of cross direction (CD) tear strength. The sample with all in-house repro appears to have somewhat better properties than the one made with commercial repro. The commercial repro used in this study was from a different source than the material used in the monolayer films. In the coextruded films, there was no significant increase in unmelts in films made with the commercial repro.

The data in Table 4 show an experiment with a different grade of film. This uses only 10% repro in the center layer (5% of film). It again shows no significant degradation of film physical properties.

## Conclusions

It is shown by the data presented in this article that it is feasible to make VCI packaging films using repro resins with no or minimal compromises in physical properties. Films containing up to 20% repro were demonstrated. In-house produced repro is generally superior due to its contribution of VCI to the final product, along with better consistency and generally reduced levels of contamination. From a cost perspective, commercial repro is generally about half the price of virgin resin. In-house repro can be significantly lower in cost, depending on the specific equipment used and local labor costs.

One further advantage of in-house reprocessing is the elimination of shipping; either one-way (purchase of commercial repro) or two-way (shipping scrap to the preprocessor and the return transit of the repro to the film facility). This produces significant environmental advantages in addition to the cost savings. The structure of coextruded films makes them especially well suited for incorporation of repro, as it can be "buried" in the middle layer with even less effect on bulk physical properties and VCI performance. Depending on the quality of in-house repro, it is likely that loading levels significantly greater than 20% can be achieved with good processability and film performance.

## Acknowledgements

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## References

1 B. Miksic, R. Boyle, B. Wuertz, NACE International 2004 F.N. Speller Award Lecture:

**TABLE 4. COEXTRUDED FILMS**

Property		Units	No Repro	10% Repro (Mid Layer) In House
Caliper	—	µm	100	100
Breaking Factor	MD	N	59.76	60.25
	TD		61.83	58.92
Tensile Strength at Break	MD	MPa	24.13	23.25
	TD		26.70	24.89
Elongation at Break	MD	%	448.00	432.60
	TD		949.40	928.50
Tear Strength	MD	mN	5,127.36	4,604.16
	CD		16,847.04	16,376.16
Impact Puncture	—	N	19,567.68	19,724.64
	—	J	1.69	1.70
Coefficient of Friction	Kinetic	—	0.22	0.22
	Static	—	0.24	0.24

"Efficacy of Vapor Phase Corrosion Inhibitor Technology in Manufacturing," *Corrosion* 60, 6 (2004): pp. 515-522.

2. V.A. Goldade, L.S. Pinchuk, A.V. Makarevich, V.N. Kestelman, "Films Incorporating Corrosion Inhibitors," *Plastics for Corrosion Inhibition* (2005): pp 81-173.

3. S.M. Al-Salem, P. Lettieri, J. Baeyens, "Recycling and Recovery Routes of Plastic Solid Waste (PSW): A Review," *Waste Management* 29, 10 (2009): pp. 2625-2643.

4. F. Vilaplana, S. Karlsson, "Quality Concepts for the Improved Use of Recycled Polymeric Materials: A Review," *Macromol. Mater. Eng.* 293, 4 (2008): pp. 274-297.

5. ASTM D6988, "Standard Guide for Determination of Thickness of Plastic Film Test Specimens" (West Conshohocken, PA: ASTM, 2013).

6. ASTM D822, "Standard Test Method for Tensile Properties of Thin Plastic Sheeting" (West Conshohocken, PA: ASTM, 2002).

7. ASTM D1709, "Standard Test Methods for Impact Resistance of Plastic Film by the Free-Falling Dart Method" (West Conshohocken, PA: ASTM, 2004).

8. ASTM D1922, "Standard Test Method for Propagation Tear Resistance of Plastic Film and Thin Sheeting by Pendulum Method" (West Conshohocken, PA: ASTM, 2006).

9. ASTM D1894, "Standard Test Method for Static and Kinetic Coefficients of Friction of Plastic Film and Sheeting" (West Conshohocken, PA: ASTM, 2014).

10. ASTM F88, "Standard Test Method for Seal Strength of Flexible Barrier Materials" (West Conshohocken, PA: ASTM, 1999).

11. MIL-STD-3010, Test Method 2065, "Puncture Resistance" (Washington, DC: U.S. Dept. of Defense, 2002).

12. R.M. Patel, T.I. Butler, K.L. Walton, G.W.

Knight, "Investigation of Processing-Structure-Properties Relationships in Polyethylene Blown Films," *Polym. Eng. Sci.* 34 (1994): pp. 1506-1514.

13. K. Gillette, B. Berg, M. Kharshan, "Modern Advances in Environmentally Friendly Vapor-Phase Corrosion Inhibiting Coatings: Expanding the Realm of VpCI Packaging," *CORROSION* 2009, paper no. 09486 (Houston, TX: NACE International, 2009), p. 14.

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