Polypropylene performance in thermoform/fill/seal applications

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ABSTRACT: Resin selection for horizontal form/fill/seal applications is very end-use specific.

KEYWORDS: Heat sealing, hot forming, packaging materials, performance evaluation, polypropylene, and variables.

Polypropylene exhibits many attributes that lead to its broad use in packaging. It is generally clear and reasonably heat resistant. Furthermore, it provides an excellent barrier to moisture. Examples of polypropylene packaging include specialty pasta, luncheon meats, sausages and wieners, syringes, condiments, and single-service containers—predominantly clear containers.

A study was conducted to characterize the performance of polypropylene in one type of packaging equipment used for the applications listed above. Thin-sheet products were produced from various commercial Escorene® polypropylenes. The sheets were subsequently tested on Multi-Vac® and Tiromat® horizontal form/fill/seal lines (also designated thermoform fill and seal). Resin variables considered were melt flow rate (MFR), molecular weight distribution (MWD), nucleators/clarifiers, and ethylene content. Packaging line performance was studied via full factorial experimental design and ad hoc determination of the operating window, i.e., the minimum and maximum forming temperatures (T_{min} and T_{max}, respectively).

The following conclusions emerged:

- Lowering MFR broadens the operating window by lowering T_{min}.
- CR'ing broadens the operating window by lowering T_{min}.
- Ethylene addition lowers the optimum forming temperature (T_{opt}) proportionately to melting peak. However, T_{max} may be lowered more than T_{min}, narrowing the operating window.
- Nucleators/clarifiers raise forming temperatures, raising the T_{min} disproportionately, resulting in a narrowed window.

Package requirements

This study was targeted to food packaging applications. The primary requirements of such a package include:

- Rigidity in storage and handling conditions
- Clarity (usually). Some packages may be tinted or pigmented depending on the appearance of the contents or on unusual circumstances with regard to the contents or handling.
- Toughness—not brittle in fill/transport/use
- Barrier—moisture or gas barrier, or both
- FDA compliance and organoleptic neutrality
- Reasonable pricing.

Stiffness

Rigidity in polypropylene is directly related to crystallinity of the sheet. This, in turn, is a function of the quench conditions and resin characteristics. Slower quenching allows the formation of a higher percent crystallinity, which leads to an overall stiffer sheet. The addition of nucleators/clarifiers increases the concentration of nucleation sites, leading to a higher percent crystallinity. Generally, this leads to a stiffer sheet.

Crystallinity can be reduced with the addition of disruptions along the chain backbone. Ethylene is frequently added to polypropylene for this purpose and is quite effective. One way of describing stiffness is resistance to heat deflection as measured by heat deflection temperature (HDT). The addition of 6 wt% ethylene randomly along the backbone can reduce the HDT by as much as 75°C (**Fig. 1**).

Clarity

Clarity in a polypropylene sheet is determined primarily by average spheru-

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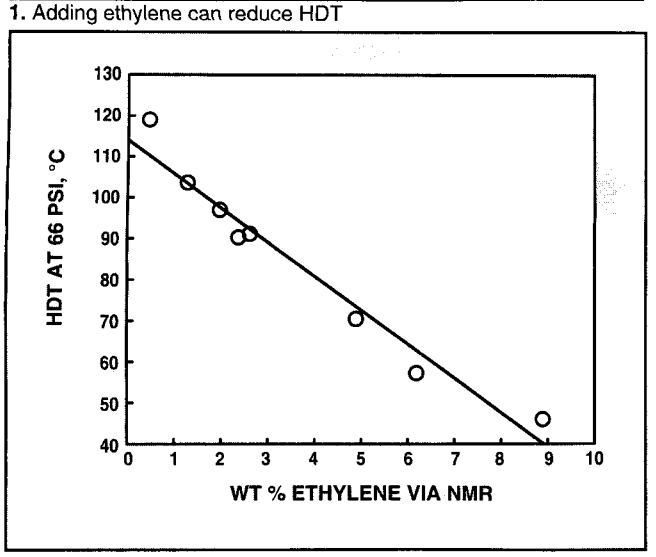
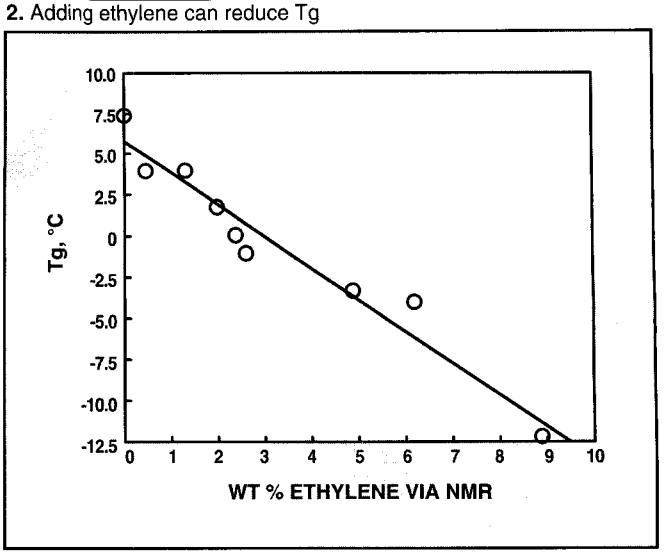
1. Adding ethylene can reduce HDT



2. Adding ethylene can reduce Tg



lite size (paper spherulites scatter light more effectively than smaller ones and cause poorer clarity). Average spherulite size is determined by the competition between spherulite rate of growth and spherulite nucleation rate according to the equation:

Average spherulite size = k(rate of spherulite growth/rate of spherulite nucleation)

Small spherulite size and high clarity are favored by:

- Fast cooling rate. The ratio above decreases as cooling rate increases, i.e., nucleation rate has a greater temperature coefficient than growth.
- Chain disruptions, which decrease the rate of spherulite growth without affecting spherulite nucleation rate
- Clarifier/nucleator, which increases the rate of spherulite nucleation without affecting spherulite growth rate.

Using PD3445 (35 MFR homopolymer) as a base material, comparisons were made with PD-9355 (35 MFR, narrow MWD copolymer with 3 wt% ethylene) (**Table I**). The ethylene addition lowered haze from 46.2% to 20.1%. A further reduction in haze to 14.7% was achieved with the addition of a nucleator/clarifier (2500 ppm Millad 3905). The clear polypropylene sheet (CPPS) yielded a haze of 10% at a similar thickness. Therefore, the ranking of clarifying effectiveness for polypropylene has

Fast quench >> ethylene addition > clarifier/nucleator.

Except for the addition of clarifiers/nucleators, clarity and stiffness tend to be opposing characteristics. Techniques that improve clarity lower stiffness. Consequently, these properties will be balanced according to the needs of the specific application.

I. Comparisons were made between several resins

Resin	*Ethylene*	*Clarifier*	*Haze, %*
PD-3445	No	No	46.2
PD-9214E1	Yes	Yes	14.7
PD-9355	Yes	No	20.1
CPPS	No	No	10.0

II. Test resins selected

Grade	*MFR*	*CR'd*	*Clarified*	*Ethylene*
PD3435G	70	No	No	No
PD3345E5	33	No	No	No
PD-3445	35	Yes	No	No
PD-9214E1	30	Yes	Yes	Yes
PP-4193	7.3	Yes	No	No
PD-9355	35	Yes	No	Yes
PD-4323	7	No	No	No
PD-5052	1.3	No	No	No
PD-040	1.3	No	No	No
XPP-323	7.3	Yes	No	No

Toughness

Polypropylene is, by its very nature, a relatively tough material. Its limitations come with low-temperature applications where the handling and use

III. The data were analyzed on a resin by resin basis

Resin	Adj. R^2 coefficient	Var. 1/t value coefficient	Var. 2/t value
PD-3435G	0.781	Depth/3.374	Form temp./7.515
COV		14.882	–0.621
Range	0.757	Form temp./1.6	Form temp. 2/2.1
		0.383	-0.002
PD3345E5	0.814	Depth/7.4	Form temp./11.6
COV		16.882	–0.494
Range	0.808	Form Temp/1.9	Form Temp 2/2.8
		0.272	–0.002
PD-3445	0.892	Depth/7.7	Form temp./10.8
COV		15.436	–0.408
Range	0.782	Form temp./0.1	Form temp. 2/0.7
		0.026	–0.001
PD-9214E1	0.246	Insignificant	. . .
COV		. . .	. . .
Range	0.248	Form temp./2.6	Form temp. 2/2.5
		–0.872	0.003
PD-9355	0.225	Depth/0.622	Form temp./2.8
COV		–3.339	0.279
Range	0.418	Form temp./0.7	Form temp. 2/2.3
		–0.284	0.002
PP-4323	0.189	Form temp./1.6	Form time/2.1
COV		0.215	3.093
Range	0.345	Form temp./3.5	. . .
		0.084	
PP-5052	0.252	Form temp./2.1	Form time/2.2
COV		0.226	2.704
Range	0.239	Insignificant	. . .
PD-040	0.126	Insignificant	. . .
COV		. . .	. . .
Range	0.148	Insignificant	. . .
XPP-323	0.334	Form temp./1.9	Form time/1.8
COV		0.577	2.986
Range	0.212	Insignificant	. . .

conditions may approach the glass transition temperature (Tg) of the resin. Examples include refrigerated containers. If the refrigeration temperature approaches Tg, the container may undergo brittle failure with even a minor impact. Glass transition is a function of rigidity along the backbone and the molecule's inability to "adapt" and absorb shock. As with stiffness, the solution is the addition of ethylene. Other studies have shown the Tg to be lowered as much as 20°C with the addition of up to 6 wt% ethylene (**Fig. 2**). As in the clarity and stiffness balance, toughness also will need to be balanced with stiffness.*

An alternative for improving toughness is the addition of elastomeric domains in the polymer matrix. The resulting two-phase material has more ability to absorb impact without brittle failure; in essence, the "shatter" is only between elastomeric domains. Generally, the stiffness of these two-phase materials is close to that of the matrix polymer. Because of the two-phase nature of the materials and the differences in the refractive indices of the two phases, these resins are hazy. This limits their usefulness in some applications.

*Davis, D. S., TAPPI 1991 Polymers, Laminations and Coatings Conference, TAPPI PRESS, Atlanta, p. 345.

FDA and organolepsis

Polypropylene is broadly compliant with U.S. Food and Drug Administration requirements—even at high temperatures—making it an ideal material for food packaging. Furthermore, efforts with the Exxon Center for Package Interaction polypropylene product line have lead to minimal interaction with most foodstuffs. This is very important for sensitive (bland) foods and for long-shelf-life items.

Barrier

Polypropylene is an excellent moisture barrier—an important feature for most packaging applications. While it is not a good oxygen/gas barrier, its moisture barrier is valuable for protecting gas-barrier resins such as ethylene vinyl alcohol. Furthermore, tie resins have been developed for polypropylene with most oxygen barrier materials.

Horizontal form/fill/seal packaging equipment

The horizontal form/fill/seal packaging line is very similar to a small thermoforming line with filling equipment incorporated, followed by a lidstock sealing system and trim station. The sheet is softened between sandwich heaters, which actually contact the sheet surface (unlike the radiant heaters of large-scale conventional thermoformers). Up to three such heater stations are used to achieve adequate heat transfer, depending on the line speed.

Containers are formed in a forming station via vacuum with plug assist. The plug assist is necessary for adequate thickness distribution in the relatively "stiff" polypropylene. Containers are cooled in the mold at the forming station.

Following deposition of the contents into the package, the lid stock is sealed to the container. This deposition/sealing station may also include gas flush or vacuum, depending on the particular application. Finally, the package is die-cut and trimmed from the web and stacked or otherwise prepared for shipping.

Test resins

Commercially available resins were selected according to availability and are shown in **Table II**.

Extrusion

All sheet samples were produced on a Black-Clawson cast-film line. Samples were extruded at 15 mils (375 μm) and slit to widths appropriate for the specific packaging line. The last sample, SPP-323 (clear polypropylene sheet), was produced via a proprietary process at 300 μm. All sheet samples were allowed to equilibrate at least two weeks before forming.

Forming trials on the Multi-Vac

All samples were formed on the Multi-Vac line at Exxon's Machelen Technical Center. The conditions were prescribed according to full factorial design, with forming temperatures of 100–160°C, forming times of 0.5–5 seconds, and draw ratios of 1.45–2.6. The higher temperatures are typical of formed containers; the lower temperatures are typical of vacuum skin packaging (VSP). In VSP, the filling station is effectively inverted. The contents are deposited on the "lid stock" and the softened "bottom web" is draped over the contents. A vacuum is pulled such that the web appears to be a skin over the contents. Here, the goal is to have minimal distortion of the web thickness, minimal "forming."

Techniques

Several containers were produced under each set of conditions. Sets of five were tested for thickness at 11 points on the container, including:

1. The side wall in the corner of the container
2. The thinnest point in the corner
3. The midpoint between points 2 and 4
4. The geometric midpoint of the container
5. The point diagonally opposite 3
6. The point diagonally opposite 2
7. The point diagonally opposite1
8/11. The thin points on the shoulder at the midpoint of the long side
9/10. The midpoints between 4 and 8 or 11, respectively.

Given the large amount of raw data (over 10,000 thickness measurements), we analyzed it using Taguchi-type techniques. The range and coefficient of variation (COV) was determined for each set of forming conditions for each sheet sample. These statistics were then correlated with resin/extrusion characteristics.

Results

Various approaches were taken to analyze the data. Software included RS/1® and Statview®. First the entire data set, including all resin characteristics and thickness characterizations, was analyzed using stepwise regression. Using an F value of 4 for removal or entry, one is left with MFR, forming time, and depth as the significant variables, in that order of influence. The final R^2 is not at all good (0.103), indicating much more variability than can be statistically associated with the design variables. MFR was a much more influential variable than either forming temperature or forming time. Because so much variability remained unexplained by this analysis, the data was analyzed on a resin-by-resin basis, considering the experimental design for each sheet sample (**Table III**).

Forming trials on the Tiromat

Forming trials were conducted for each of the resins on a Tiromat machine at T. W. Kutter. The test design here was quite different, establishing the optimum forming conditions for each resin and establishing the operating window. Generally, the minimum temperature was that temperature at which the thin shoulders and corners became acceptably thick. The maximum temperature was associated with the sheet or web becoming molten and sagging between stations. The PD-040 resin was somewhat unique in that it failed at high temperatures because it picked up too much of the pattern from the sandwich heaters. The data are shown in **Table IV**.

Many horizontal form/fill/seal (HFFS) operations are conducted in small-scale settings. Operators are kept busy with the multiplicity of raw materials: bottom web, top web, and package contents. The electronics may be poorly maintained, resulting in broad variability. For these reasons, it is particularly important for the operating window to be broad—typical of a "forgiving" process.

Effect of MFR on the window

Overall, the effect of lowering MFR was to broaden the operating window by lowering the T_{min}. For homopolymers such as PD3435G, PD3345E5, PP-4193, and PP-5052, T_{max} remained constant at 165°C, about the melting point above which the sheet was not softened but molten. Above those temperatures, the sheet sagged and was not usable in the HFFS process. Similarly, the optimum temperature was just a few degrees cooler than this maximum. The difference was in the T_{min}. Given this observation, it is pos-

IV. Data from Tiromat trials

Resin	T_{max}, °C	T_{min}, °C	T_{opt}, °C	Window, °C
PD3435G	165	159	162	6
PD3345E5	165	153	163	12
PP-3445	165	140	155	25
PD-9214E1	147	137	142	10
PP-4193	165	140	160	25
PD-9355	145	130	140	15
PP-4323	165	145	160	20
PP-5052	165	155	160	10
PD-040	165	155	155	10

sible that the effect is due to crystallinity in the sheet. As the MFR increases, so does the crystallinity. This requires more heat to soften the sheet to avoid thinning.

On the other hand, if one is using the polypropylene in a skin packaging application, where minimal softening is desired, the higher-MFR material is more appropriate. In these applications, avoiding permanent deformation of the sheet during packaging leads to maximum recovery and thickness uniformity after vacuum or shrink, or both.

Hence, the resin choice will depend on which mode of operation is selected: for traditional HFFS, lower MFRs are preferred; for skin packaging, higher MFRs are preferred.

Effect of CR'ing on the window

Narrowing the MWD of a resin via the CR process broadens the operating window by lowering the T_{min}. This trend is observed with PD-3345E5 versus PD-3445 and PP-4193 versus PP-4323. The trend is consistent with other observations: CR'ing lowers stiffness, it clarifies, and it lowers the softening point and heat deflection temperature.

Effect of ethylene addition on the window

Comparison of PP-3445 and PD-9355 indicates that the addition of ethylene lowers the T_{opt} proportionately to the melting point depression. However, the Tiromat test indicated the T_{max} and T_{min} were lowered proportionately with the addition of ethylene, resulting in a narrowed operating window. This phenomenon is not fully understood. The ethylene copolymer does not soften at the low temperature predicted; however, it becomes fully molten, losing melt strength at a lower-than-predicted temperature. In previous work,* I have shown that ethylene addition lowers melting peak more than crystallization peak. Perhaps this phenomenon is affecting the forming window.

The primary effect of adding nucleators or clarifiers to the sheet is to increase the crystallinity. The sheet becomes stiffer and more brittle, and the softening point is raised. The T_{min} is raised 7°C in the example cited, resulting in a significantly more narrow window. The T_{max} is more dependent on complete melting; consequently, it is little affected by the nucleation. The T_{opt} is raised slightly, comparable to the T_{max}.

MWD effect on the window

The MWD effect on forming was tested with PP-5052 and PD-040. Both have the same MFR (1.3), but PD-040 is intentionally broadened for better melt strength. In this particular test, the enhanced melt strength was offset by a softening of the surface such that, at high temperatures, the surface took on the texture of the sandwich heaters. This was perceived to be an unacceptable visual defect. This imprinting began at 160°C, which was lower than the maximum forming temperature for PP-5052, so it narrowed the window. T_{min} was the same for both samples, indicating that there was no significant difference in the softening point and crystallinity of the two resins.

Conclusions

Resin selection for HFFS applications is very end-use specific. While there are some generalities, such as the desirability of a broad operating window, other performance criteria are balances of various attributes. Keeping this in mind, the following conclusions are made:

- Lower MFR is better for horizontal form/fill/seal; higher MFR is better for skin packaging.
- CR'ing broadens the window.
- Nucleators/clarifiers and ethylene addition lower haze but narrow the forming window. ■

Several people at Exxon's Machelen Technical Center were instrumental in the Multi-Vac trials, including Pierre de Wagoneer, Guy Bayers, Brigitte Leroy, and Wilfried van Craeynest. The staff at T. W. Kutter not only executed the Tiromat tests but also provided valuable insights on the process itself. Claude Watkins at the BPC measured thickness on all the containers for analysis.

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