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# VINYL CHLORIDE-ETHYLENE COPOLYMERS FOR PACKAGING

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Polyvinyl chloride possesses some excellent characteristics for use as a packaging material. These include a combination of strength, rigidity and clarity, good chemical resistance, low permeability to water, oxygen, flavor and odor essences. Of the common packaging materials shown in Table I, rigid PVC has the best combination of barrier properties. However, rigid PVC accounts for less than 6% of the total volume of plastics consumed in packaging in this country during 1967. Three factors have inhibited PVC's penetration of the packaging market:

Limited heat stability
Lack of FDA sanctioned additives
Cost

To better understand the nature of these limiting factors a look at PVC formulating and processing is in order. Table II is a simplified account of the ingredients common to impact grade rigid PVC formulations. The stabilizers (generally organometallics) provide thermal protection for the polymer preventing discoloration, chain scission or cross linking. The process aids are to produce the hot strength necessary for even wall distribution and low parison sag in blow molding and drawability in vacuum forming. The flow aid also eliminates melt fracture and promotes efficient mixing in the extruder. The impact modifier gives the added toughness required for commercial containers. The lubricants prevent excessive heat generation from frictional working and polymer adhesion (stagnation) to the processing equipment which would lead to thermal degradation.

In order to overcome the cost limitations of present PVC formulations a minimization of the most expensive additives is necessary. Stabilizer costs can be further broken down by stabilizer categories. The least expensive but also least effective type are the FDA approved calcium-zinc combinations ranging from \$.50 – \$1.00/lb. The octyl tins require extraction testing for food applications and are much more effective but cost over \$3.00/lb. The most widely used stabilizers for rigids are butyl tins; these are very effective and cost from \$1.75 – \$2.50/lb but lack FDA approval.

Figure 1 illustrates the thermal stability of a food packaging grade (calcium-zinc) stabilized clear rigid PVC as a function of temperature.

The ordinate plots stock temperature in the rolling bank of a high speed mill while the abscissa plots time to yellowing of the polymer melt. The conditions of this test are felt to represent polymer history in the die section of blow molding equipment. This curve may shift for various shear rates (4500 $sec.^{-1}$ in this case), different formulations and the presence or absence of oxygen but the trend is undeniable with higher temperatures causing faster yellowing.

A given fabrication process requires a minimum residence time during which the polymer remains at an elevated temperature, this residence limits the maximum permissible stock temperature. As an example a 3 minute residence time requires a stock temperature of 365°F or lower.

Figure 2 illustrates the effect of the PVC molecular weight (inherent viscosity) on melt viscosity (here referenced by Brabender Torque*) and therefore on the stock temperature necessary to extrude sheet or blow mold. As expected the higher molecular weight resin with its greater melt viscosity requires and develops higher stock temperature for extrusion. Continuing our example of a three minute residence time requiring a 365°F stock temperature, a PVC resin with inherent viscosity of 0.70 or less must be used. It is now obvious that for a given stabilization system and a particular fabrication process the molecular weight of the PVC resin is limited below a certain level for adequate processability (i.e., absence of polymer degradation).

To carry our first example to its conclusion the fixed resin molecular weight predetermines the physical properties of the fabricated item.

*The Brabender Torque values were determined on the No. 6 bowl at 168°C jacket temperature and 40 RPM with a 56.4 charge. The stock temperatures are for a 2½" two stage extruder at 20 RPM.

Perhaps the most significant physical property for bottles is impact strength. Figure 3 shows the break resistance of 8 oz. bottles plotted as the height for 50% failure on the ordinate versus the inherent viscosity of the base PVC resin on the abscissa for 12% impact modifier. In our example the 0.70 inherent viscosity resin will limit impact to a 5 ft. height for 50% failure with the 8 oz. bottle. Let's consider what has been achieved; a food grade container with a fair impact strength but a relatively high concentration of impact modifier. Please remember that these values are relative since choice of stabilizer, lubricant, impact modifier and bottle design all affect impact strength. The selection of a three minute residence time may be optimistic or conservative depending on equipment.

If greater impact strength is desired a potential solution would be the addition of more impact modifier. However, as impact modifier concentration increases several adverse effects occur as illustrated in Table III. In the interest of cost, clarity, permeability, heat stability and chemical resistance, it would be desirable to reduce the necessary impact modifier concentration, but use of increased molecular weight resin is prohibited by thermal stability. Another solution would be the use of a tin stabilizer which would provide better resistance to yellowing under heat. This approach is currently used in the general purpose bottle market but tins are more costly, can be odoriferous and require extraction testing.

These limitations have hindered the penetration of rigid PVC in the packaging market.

Copolymers of vinyl chloride and ethylene offer solutions to the restrictions of limited heat stability, use of FDA sanctioned additives and formulation costs that presently retard use of rigid PVC.

Figure 4 shows the effect of the ethylene comonomer in reducing the melt viscosity and stock temperature necessary to fabricate containers for any given molecular weight of resin.

It is important to emphasize that the selection of ethylene as a comonomer is important because it does not reduce the thermal stability of the resin as vinyl acetate does, for example. Another important reason for the selection of ethylene is that it does not subtract from the ability of the resin to respond to impact modifiers. A vinyl chloride-ethylene copolymer will provide as much impact per percent of added impact modifier as a homopolymer of equal molecular weight. Recalling our example of a fabrication process with a three minute residence time which necessitated a stock temperature of 365° F or less, the use of a vinyl chloride-ethylene copolymer allows the selection of a 0.80 inherent viscosity resin instead of a 0.70 inherent viscosity homopolymer. In reviewing Figure 3 the use of a 0.80 IV resin will provide a 7 ft. height for 50% failure for the 8 oz. bottle. The homopolymer of equal precessability gave only a 5 ft. height for this same formulation. This provides two opportunities in the use of vinyl chloride-ethylene copolymers:

1. The ability to provide extra impact strength for equivalent concentrations of impact modifier.

   or

2. The ability to provide equivalent impact to the homopolymer system but using less impact modifier.

The vinyl chloride-ethylene copolymer advantages are not confined to food grade formulations. In the general purpose (butyl tin stabilized) powderblend market the same advantages of lower melt viscosity for a given molecular weight can be put to work. For example, consider the fabrication process with the 3 minute residence time once again, with the butyl tin stabilizers, perhaps a stock temperature of 420°F can be tolerated. Referring back to the stock temperature at fabrication versus molecular weight curves this would allow use of either a 0.92 inherent viscosity homopolymer or a 0.98 inherent viscosity copolymer. The higher molecular weight copolymer would require less impact modifier for equal impact. Another approach would be the use of a 0.92 IV copolymer giving equal impact to the homopolymer at the same modifier concentration but fabricating at a lower temperature and thus requiring less stabilizer.

These comparisons on paper sound good but what about proof in an actual comparison? For this purpose two powderblends were prepared using FDA approved stabilizers, impact modifiers, flow aids and lubricants. Based on our earlier hypothesis a homopolymer of 0.70 IV is used in one formulation with a vinyl chloride-ethylene copolymer of 0.80 IV used in the second. The aim is to produce systems of equal processability and impact strength and then compare properties. The copolymer formulation was also adjusted to account for the lubricity and hot strength provided by the ethylene comonomer. If the reduction in lubricant level is not made the copolymer based powderblend may be overlubricated resulting in melt fracture, less clarity and lower impact because of insufficient mixing. This illustrates that formulation must be tailored to obtain maximum benefits from the copolymer resin.

Table IV summarizes the two formulations. Note that the copolymer system has 7 percent modifier as compared to 11 percent, one percent process aid compared to 1.5 percent and 0.45 percent lubricant compared to 0.60 percent, but the stabilizer system is identical. The powderblends were fluxed on a two roll mill and subsequently compression molded. The specimens were found to have the properties listed in Table V. The copolymer system has slightly higher tensile strength, modulus and elongation. One sacrifice is made in using the copolymer and that is illustrated in the 2°C lower heat distortion temperature, but this difference is not significant in most packaging applications.

The powderblends were then characterized by Brabender and extrusion-blow molded on a 2½" two stage extruder. Table V illustrates that the desired equivalence in processability was definitely achieved. The extrusion data confirms on a practical basis the Brabender Torque values.

In powderblend extrusion the selection of screw design can have as great an effect on the processability and the properties of the fabricated item as does the formulation. The extruder performs the mixing as well as the pumping in powderblend operation, and the matching of the formulation to the proper screw design is essential in obtaining the desired level of mixing.

This mixing provides the dispersion of the additives necessary for impact strength and clarity. The experiments described in this paper were performed on an extruder with the following characteristics:

| | |
|---|---|
| Diameter | 2.500" |
| Length/Diameter | 26/1 |
| Pitch | 2.500" |
| Helix Angle | 18° |
| Radical Barrel Clearance | 0.003" |

| Section | No. of Flights | Channel Depth, inches |
|---|---|---|
| Feed | 6 | 0.380 |
| Transition | 6 | 0.380 – 0.125 |
| Metering | 3 | 0.125 |
| Vent | 4 | 0.280 |
| Metering | 4 | 0.180 |

The extruder is equipped with a vacuum hopper-stuffer to exclude air and assure uniform feed. A blister tip is used on the front of the screw to provide adequate dispersion. The blister tip has a 0.250 inch land with a radial clearance of 0.035 inch. The two powderblends shown were formulated to match the fusion and lubricity requirements of this equipment. In extruding rigid PVC powderblends, a compression ratio of 2.7 – 3.4/1 is recommended to develop sufficient mixing. If a crammer type feeder is not used, a compression ratio of 3.0 – 3.4/1 should be selected.

The bottles molded during the extrusion trial were filled to 95% level with tap water, aged for 24 hrs. at 73°F and tested to find the minimum height at which any failure would occur for one dozen bottles dropped. The results exceeded expectation as the copolymer system proved not equivalent but superior.* (See Table V).

The sample bottles blow molded in this experiment show the clarity and color achieved on an extruder designed for rigid PVC powderblend operation. The homopolymer based bottle is much yellower (beyond the limit of commercial acceptance for many applications) than the copolymer bottle in spite of equal concentrations of stabilizer and equivalent processing conditions. The superior thermal stability of the copolymer under extrusion conditions provides more tolerance for regrind and better economics in tin stabilized formulations.

Additionally, these deep draw vacuum formed samples show the superior hot strength of sheet prepared from the copolymer formulations compared to sheet from the homopolymer formulation. The copolymer had more hot strength even though less flow aid was in the powderblend. This hot strength allows deeper draws and thinner walls in vacuum forming or more consistent wall distribution and higher blow ratios in blow molding or forming at lower temperatures.

Summarizing the results of this comparison the copolymer showed:

1. Lower additive concentrations necessary for better performance than a homopolymer of equal melt viscosity.
2. Superior heat stability
3. Superior hot strength

The vinyl chloride-ethylene copolymers provide the opportunity for:

A product of useful physical properties with calcium-zinc stabilizers.

The ability to obtain "super" impact.

A lower additive requirement.

The ability of vinyl chloride-ethylene copolymers** to further alleviate the problems which have limited the penetration of PVC in packaging should open wider the doors to the packaging market for rigid PVC.

## ACKNOWLEDGEMENTS

The author gratefully acknowledges contributions to this paper by many colleagues and especially to W. P. Mayer for permeability measurements and interpretation and J. Gargiulo and N. Kirk for technical assistance in making the many measurements and samples that were necessary.

*The impact results obtained here are not comparable to the results presented earlier in Figure 3 because of different formulations, bottle shape and bottle size.

**Vinyl Chloride-Ethylene copolymers are the subject of food additive petition 8B-2275, which has been filed with Food & Drug Administration.

FIGURE 1

COLOR STABILITY VS STOCK TEMPERATURE
FDA RIGID VINYL

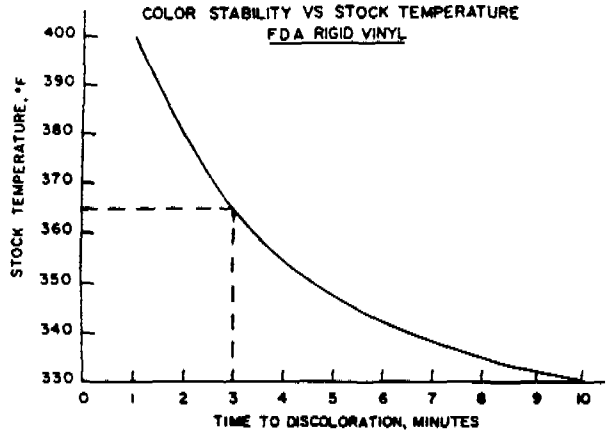


FIGURE 2

EFFECT OF PVC MOLECULAR WEIGHT
ON PROCESSABILITY

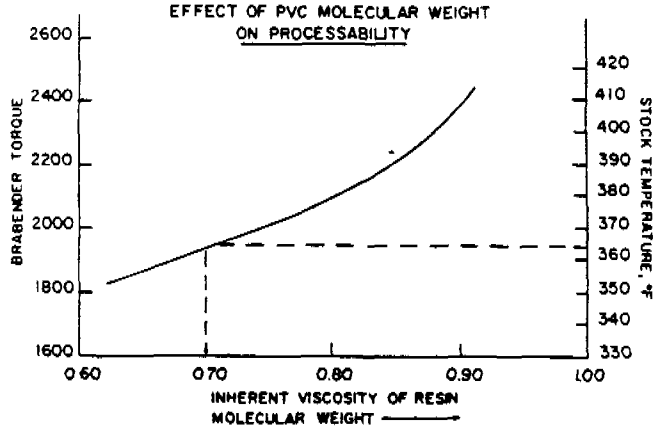


FIGURE 3

BOTTLE DROP STRENGTH VS RESIN VISCOSITY

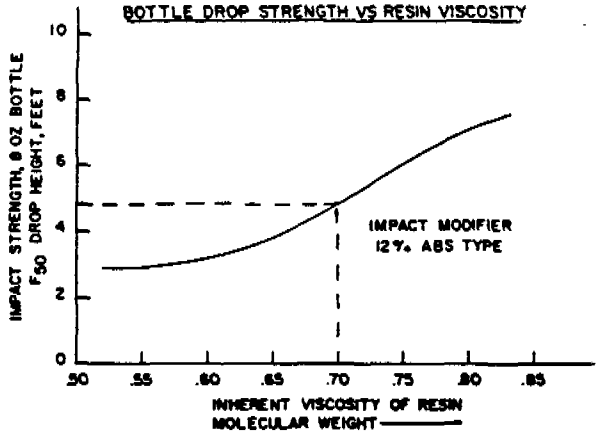


FIGURE 4

EFFECT OF RESIN MOLECULAR WEIGHT
ON PROCESSABILITY

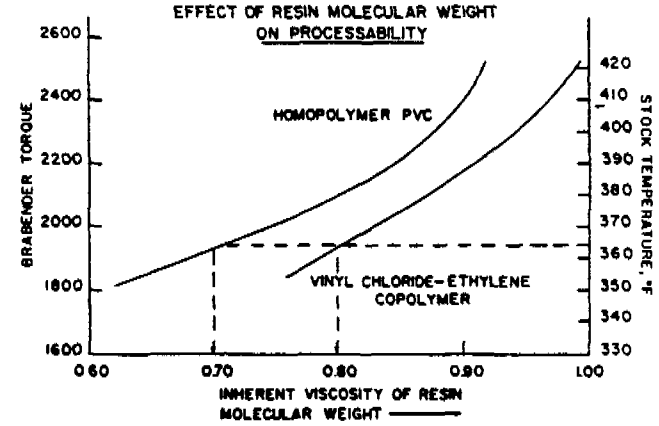


TABLE 1

COMPARATIVE BARRIER PROPERTIES

| | PERMEABILITY | | % LOSS[3] | |
|---|---|---|---|---|
| | WATER[1] | OXYGEN[2] | 2 WEEKS | 3 MONTHS |
| RIGID PVC (IMPACT GRADE) | 3.0 | 10 | 40 | 45 |
| ACRYLIC MULTIPOLYMER | 12.0 | 32 | 40 | 45 |
| STYRENE ACRYLONITRILE | 13.0 | – | 30 | 34 |
| POLYPROPYLENE | 0.97 | – | 53 | 82 |
| LDPE (0.92) | 1.65 | 350 | – | – |
| HDPE (0.95) | 0.78 | 80 | 79 | 97 |

[1] PERMEABILITY CONSTANT: GRAM MILS/100 IN$^2$, DAY AT 100°F/90% RH MEASURED AT STEADY STATE IN 4 OZ. BLOWN BOTTLES FILLED WITH DESICCANT.

[2] DOW CELL OXYGEN PERMEABILITY ASTM D1434
CC (STP) MILS/100 IN$^2$, DAY ATM.

[3] 104°F – 0.07% AQUEOUS METHYL SALICYLATE

TABLE II

IMPACT GRADE CLEAR RIGID PVC
COMPOSITION AND COST RANGES

| | WEIGHT PERCENT | COST, $/LB. |
|---|---|---|
| PVC RESIN | 73 TO 91 | |
| STABILIZER | 1.0 TO 3.0 | .50 TO 3.50 |
| PROCESS AID | 1.5 TO 3.0 | .45 |
| IMPACT MODIFIER | 5.0 TO 20.0 | 40 TO .50 |
| LUBRICANTS | 0.5 TO 1.5 | .20 TO .80 |

TABLE III

EFFECT OF INCREASING
IMPACT MODIFIER CONCENTRATION

IMPROVES IMPACT STRENGTH
INCREASES RAW MATERIAL COSTS
REDUCES CLARITY
INCREASES PERMEABILITY
DECREASES HEAT STABILITY
DECREASES CHEMICAL RESISTANCE
INCREASES MELT VISCOSITY
REDUCES TENSILE STRENGTH
REDUCES MODULUS

TABLE IV

COMPARATIVE FORMULATIONS

| | HOMOPOLYMER (0.70 IV) SYSTEM | COPOLYMER (0.80 IV) SYSTEM |
|---|---|---|
| VINYL RESIN | 82.72 | 87.37 |
| ACRYLIC IMPACT MODIFIER | 11.00 | 7.00 |
| PROCESS AID | 1.50 | 1.00 |
| CA-ZN STABILIZER | 2.14 | 2.14 |
| EPOXIDIZED SOY BEAN OIL | 2.00 | 2.00 |
| LUBRICANT | 0.60 | 0.45 |
| TONER | 0.04 | 0.04 |
| | 100.00 | 100.00 |

TABLE V

COMPARATIVE PROPERTIES

| PHYSICAL PROPERTIES | HOMOPOLYMER SYSTEM | COPOLYMER SYSTEM |
|---|---|---|
| TENSILE STRENGTH, PSI | 6240 | 6550 |
| TENSILE MODULUS, PSI | 335,000 | 343,000 |
| ELONGATION, % | 130 | 158 |
| SPECIFIC GRAVITY | 1.31 | 1.32 |
| HEAT DISTORTION TEMP. (264 PSI), °C | 63 | 61 |
| **FABRICATION PARAMETER** | | |
| BRABENDER EQUILIBRIUM TORQUE, M.G. | 2275 | 2285 |
| EXTRUSION RATE (2 1/2") LB./HR./RPM | 3.2 | 3.2 |
| STOCK TEMPERATURE, °F | 375 | 372 |
| BOTTLE WEIGHT, G. | 37.6 | 37.0 |
| **CONTAINER PROPERTIES (15 OZ. ROUND SHOULDERED OVAL)** | | |
| IMPACT STRENGTH MINIMUM HEIGHT TO FAIL, FT. | 14 | 16 |

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