# Regrind utilization in EVOH barrier structures

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*The type of polymer, processing equipment, and processing condition directly affect the generation of gels and the amount of degraded polymer buildup in the regrind extruder.*

The barrier plastic packaging revolution has grown rapidly since its birth a short seven years ago. During these years, ethylene vinyl alcohol (EVOH) has emerged as the premier barrier polymer because its gas barrier properties are superior to those of other barrier polymers. EVOH provides excellent barrier to oxygen and other gases that are important in the food packaging industry. EVOH resins are used almost exclusively in coextrusions to combine its high barrier property with relatively low-cost structural resins such as polypropylene (PP) and polyethylenes (PE). This process yields a high-performance, low-cost composite structure that is competitive with traditional barrier packaging materials such as glass and metal.

Some process scrap is generated in even the best plastic converting operations. This scrap must be reclaimed and re-used in the converting operation, if the plastic is to compete with other packaging media. In barrier coextrusion, the reclaimed resin or regrind becomes a "melting pot" of different materials that might interact. These possible interactions present new challenges and considerations not evident with single-material regrind systems.

A great advantage of EVOH barrier structures over other barrier polymers is that EVOH-based regrind can be readily reclaimed and re-used in the coextruded structure. The degree of success of such an operation depends on the measures taken to minimize the interaction between EVOH, base polymer, color concentrate, and any other material that has a tendency to find its way into the regrind system. Here, we will describe the characteristics of EVOH-based regrind and recommend measures to successfully incorporate it into the barrier structure.

## Coextrusion process and regrind

The amount of scrap generated in the converting process is determined by the process itself. **Table I** shows the various coextrusion processes in which EVOH is commonly used, along with the amount of scrap the process typically generates.

I. Various processes using EVOH coextrusion

| Process | *Scrap rates of normal production* |
|---|---|
| Blown film | < 10 % |
| Cast film | < 10% |
| Blow molding | 20-35% |
| Thermoforming | 40-60% |
| Coextrusion coating | < 10% |

The amount of scrap generated determines the means by which it is re-used in the finished product. Scrap produced in relatively small amounts, such as generated with blown and cast films, will be handled differently than scrap produced in large amounts, as in the thermoforming process. Though little scrap is generated in coextrusion coating, this scrap cannot be re-used in the finished product and must be disposed of by some other means.

### Regrind from blown and cast film coextrusions

Generally, processes generating small amounts of scrap that are reclaimed and re-used do not pose a serious problem to the converter. In these cases, the preferred method is to blend the regrind into the main polymer layer or the bulk layer of the film. The primary advantage is that this method requires only a minimal capital investment for equipment, handling systems, storage, etc. The drawback to blending EVOH-based regrind into the bulk film layer is the deterioration of the film's physical properties. **Figures 1-4** show the physical properties of PP/EVOH films. The EVOH is a 32% (by mol) ethylene copolymer resin. The polypropylene is a homopolymer resin. The film thickness is 25 $\mu$m.

Tensile strength, elongation, impact strength, and optical properties are decreased as the amount of EVOH increases for PP/EVOH-blended films. Similar trends are evident for PE/EVOH-blended films. The decrease in physical properties is attributable to the incompatibility of EVOH and polyolefins in general. However, the

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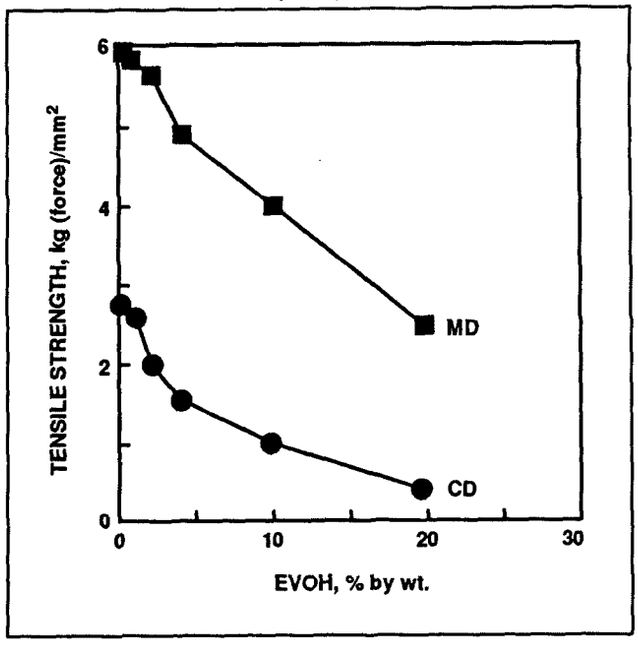
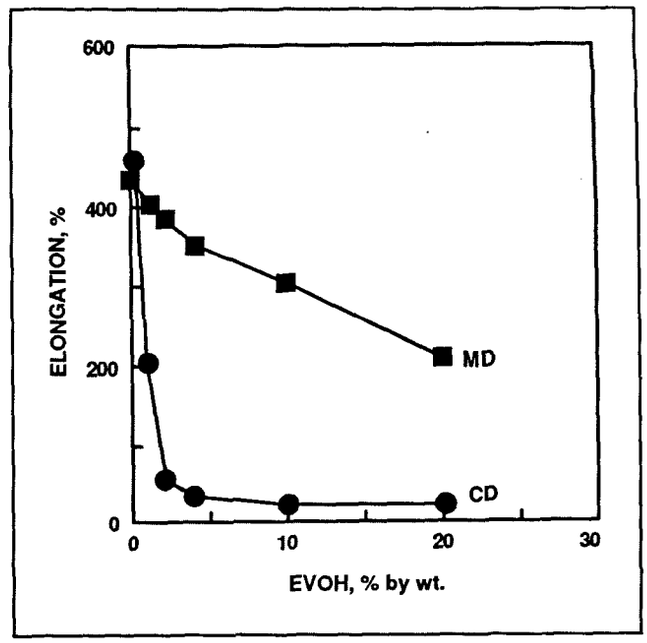
1. Tensile strength of PP/EVOH-blended films (where tensile strength is measured in force divided by area)




2. Elongation at break of PP/EVOH-blended films




presence of adhesive resin will tend to make the mixture compatible to some degree.

At first glance, the decrease in physical properties of EVOH/polyolefin-blended films may appear to be a deterrent to using EVOH-based regrind in the bulk layer of the film. Fortunately, this is not the case. The EVOH concentration in polyolefin/EVOH films is usually quite low. The equilibrium concentration in the bulk layer of the film can be calculated by using Eq. 1.

$$e = 1 / (1 + 1/RE - 1/R - 1/E) \quad (1)$$

where

$e$ = weight fraction of EVOH in the bulk layer of film

$R$ = scrap rate or weight fraction regrind in the bulk layer of film

$E$ = weight fraction of virgin EVOH layer.

For example, a typical 30-$\mu$m PP/EVOH coextruded film would have an EVOH thickness of 3.0 $\mu$m. Assume that the scrap rate is 10% ($R$ = 0.10). Accounting for the density difference between PP and EVOH (PP = 0.89 g/cm$^3$, EVOH = 1.19 g/cm$^3$) gives a weight fraction of virgin EVOH of 13% ($E$ = 0.13). Substituting the values of $E$ and $R$ into Eq. 1 gives an equilibrium concentration of EVOH in the bulk layer of 1.6%. Referring to Figs. 1-4, only a minimal decrease in physical properties is realized at such a low EVOH concentration.

Despite the relative ease and low cost of blending EVOH-based regrind back into the bulk film layer, this method is seldom used in commercial practice. If the packaging is for food, virgin resins are preferred as the food contact layer. Often, the EVOH-based regrind is used elsewhere in the film plant in a product that will not be used for food packaging.

**Regrind from thermoforming and blow-molding coextrusions**

Processes generating moderate to large amounts of scrap to be reclaimed and re-used pose a more challenging task to the converter. In this case, a separate regrind extruder and a more complex die and feedblock are required to re-use the EVOH-based regrind and extrude it into its own distinct layer. This method of regrind is often referred to as the "sandwich" method since the regrind is sandwiched between two outer layers of virgin resin. The advantage of the sandwich method is the preservation of a "clean" food contact surface and mitigation of the effect that regrind has on the physical properties of the finished product.

With the sandwich method, the amount of regrind that can be re-used in the barrier container is a function of many factors. The equilibrium weight fraction of EVOH in the regrind is one such factor and can be calculated by using Eq. 2:

$$e = E/ (1 - R) \quad (2)$$

where

$e$ = weight fraction of EVOH in the regrind layer

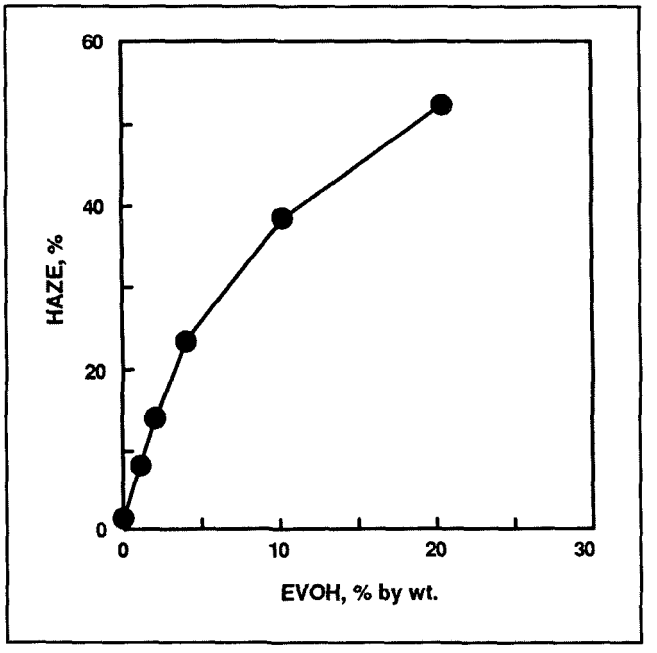
$E$ = weight fraction of virgin EVOH

$R$ = scrap rate or weight fraction of regrind.

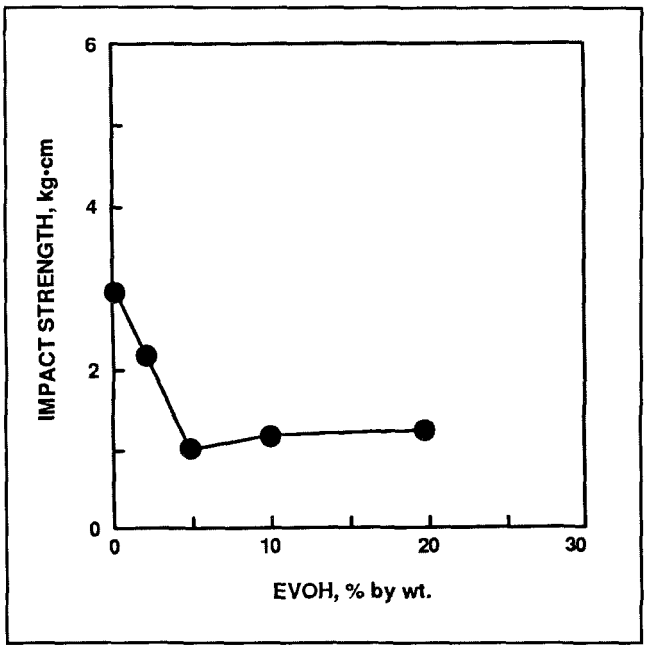
Equilibrium is usually achieved after seven regrind passes. Keep in mind that Eq. 2 is used for the sandwich method of regrind use. Equation 1 is used for the blend method.

For example, a typical 222-mL (7.5 oz.) 307, double-seam, retortable container is a PP/adhesive/EVOH/adhesive/PP structure having a total average wall thickness of 762 $\mu$m (30 mils). The EVOH thickness is about 6.35 $\mu$m (2.5 mils). Correcting for density differences, the weight fraction of virgin EVOH is 10% ($E$ =

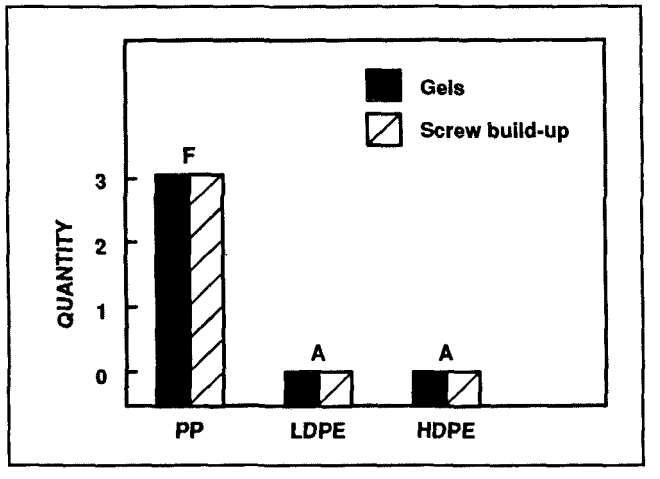
3. Haze for PP/EVOH-blended films




4. Impact strength of PP/EVOH-blended films




5. Thermal stability of EVOH/polyolefin blends (LDPE = low-density polyethylene. HDPE = high-density polyethylene.)




0.10). Assume the scrap rate of the thermoforming process is 50% ($R = 0.50$). This gives an equilibrium weight fraction of EVOH in the regrind layer of 20% ($e = 0.20$). No more than a short three years ago, it was believed that the maximum weight fraction of EVOH in the regrind layer was 15%. However, this percentage has increased to as high as 25% through advances in equipment design, improved additives, and a better understanding of the factors that affect regrind degradation.

## Factors affecting regrind utilization

The factors that affect successful regrind utilization generally are the same for EVOH-based regrind and traditional monolayer systems. Equipment, processing conditions, and the type of polymers and additives used must all be considered. Successful use of EVOH-based regrind can be achieved by producing a homogeneous melt stream and by minimizing regrind degradation. The means necessary to generate a homogeneous melt are fairly well known throughout the industry and do not differ greatly from the means of normal polymer processing.

Minimizing regrind degradation is a different story. Multilayer regrind typically contains polyolefin, extrudable adhesive resin, EVOH, and color concentrates. Considered separately, all these materials are usually thermally stable and will not degrade under normal processing conditions. When mixed in a regrind stream, these materials can interact, resulting in bottles or sheet of poor quality.

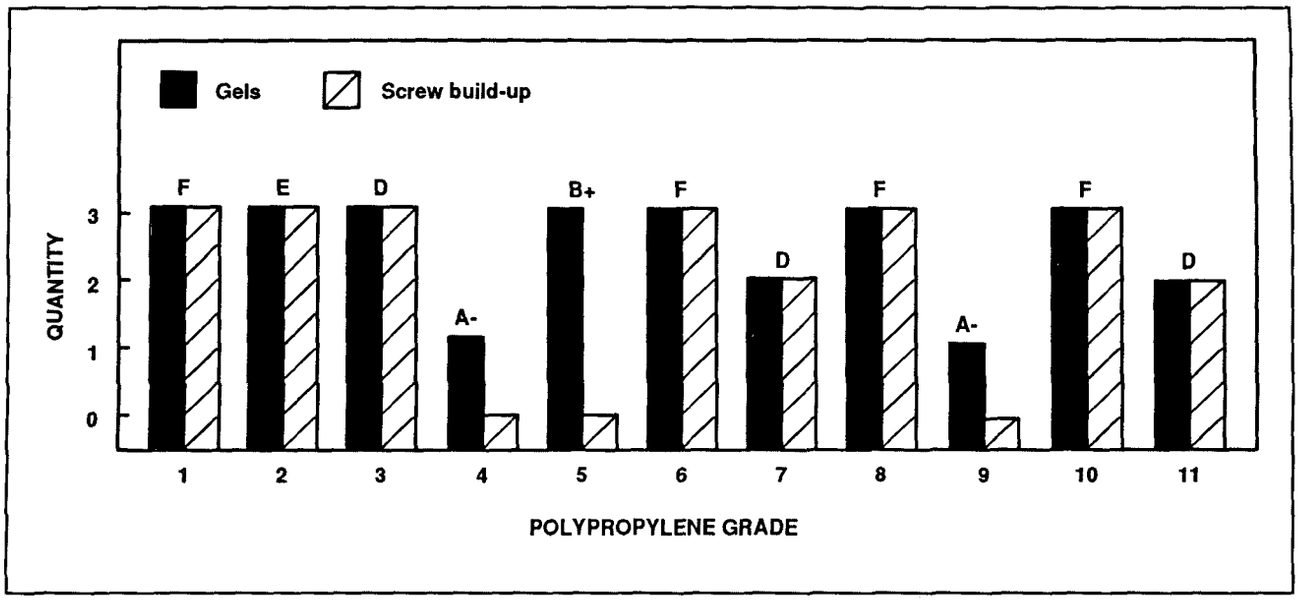
### Thermal stability of regrind

Maintaining the thermal stability of EVOH-based regrind is one of the most important considerations in successfully incorporating it into a high-quality barrier structure. Unstable regrind manifests itself in poor quality bottles and sheet and is evident in "applesauce" patterns, melt flow lines, "ocean waves," gels, and degraded polymer buildup on processing equipment.

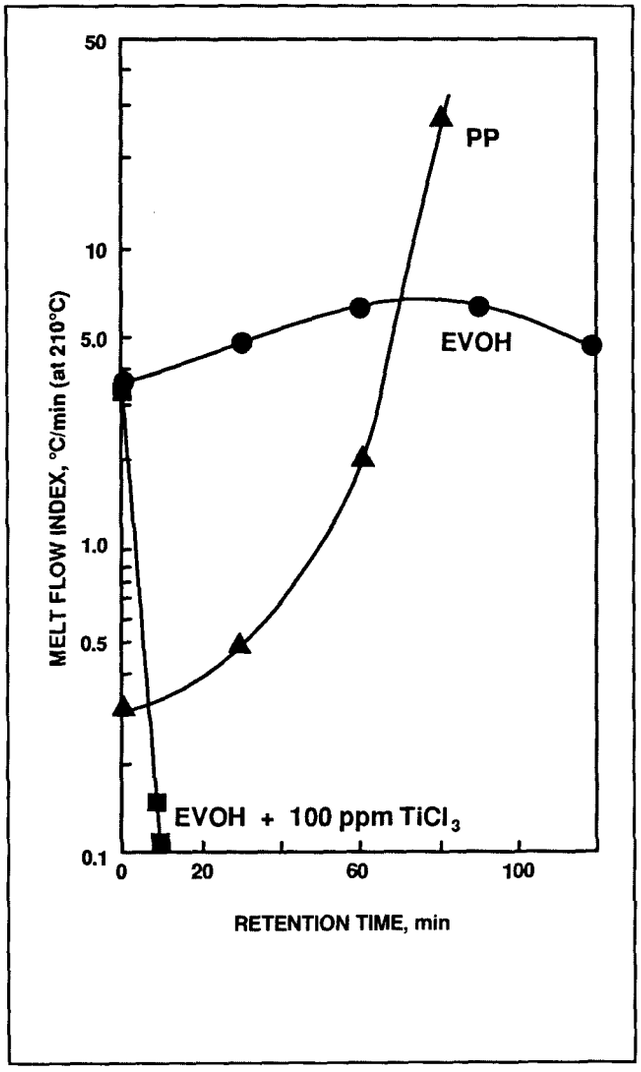
We conducted experiments to determine the effect of polyolefin type, EVOH content, and "white concentrate," which is the same as $TiO_2$ masterbatch. For all evaluations, we used extruded films (about 100 $\mu$m thick) rather than sheet because gels are easier to recognize in film than in sheet. The EVOH resin used in all instances was a 32% (by mole) ethylene copolymer with a melt index of 1.6 (in centigrade degrees/min at 190°C). Higher-than-normal extrusion temperatures (230-250°C) were used to promote regrind degradation.

Films were evaluated for gel count, and the extruder screw was analyzed for degraded polymer buildup. In the figures, the quantities for both gel count and buildup are given on a scale of 0-3, where 0 = none, 1 = slight, 2 = moderate, and 3 = heavy. A qualitative grade or ranking

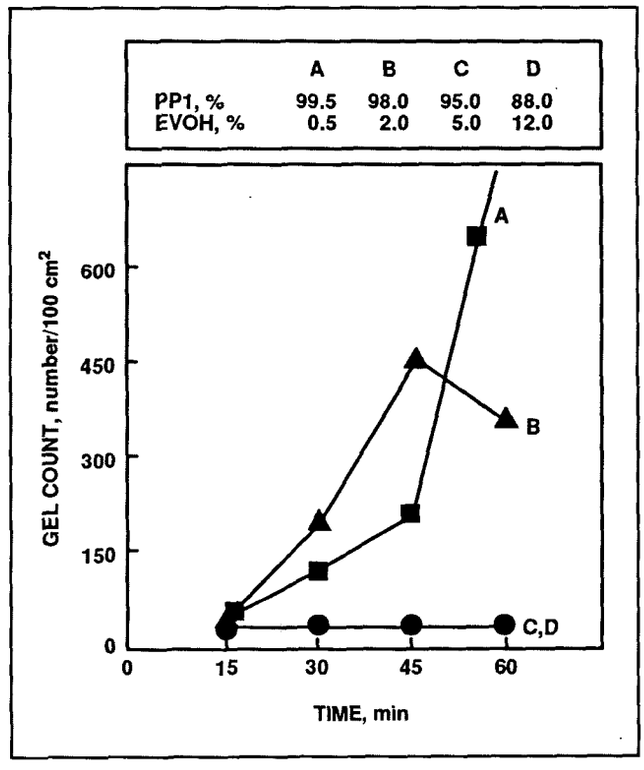
6. Thermal stability of PP/EVOH blends (99.5% polypropylene and 0.5% EVOH)




7. Thermal stability of EVOH, PP, and EVOH+ $TiCl_3$ (retention in mixer at 200°C)




8. Gel frequency for various blends of EVOH and PP

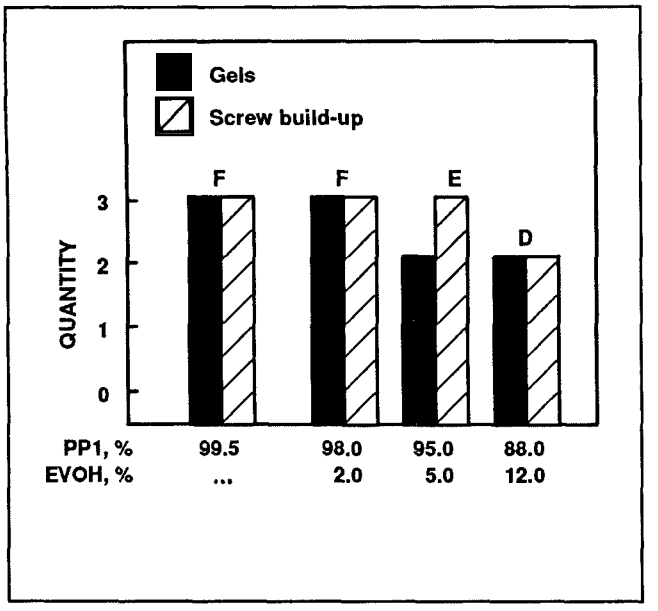



was assigned to each film for comparative purposes. The grade scale used was A through F, with A being best and F being worst.

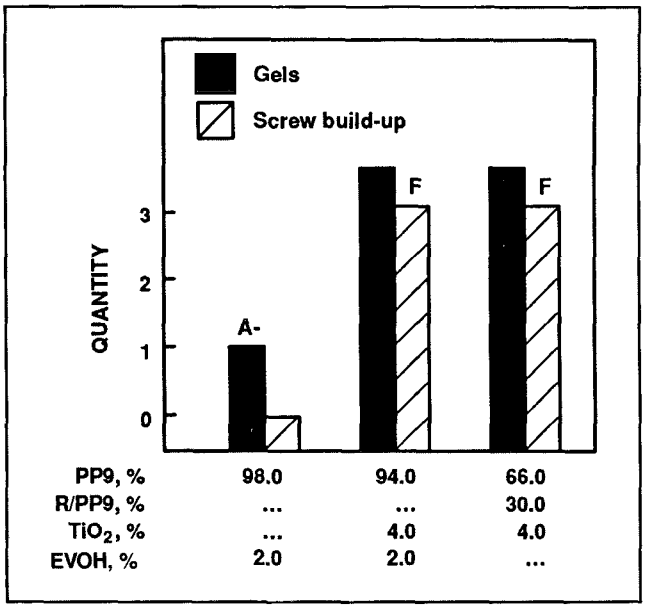
### Effect of polyolefin type

Polypropylene, low-density polypropylene (LDPE), and high-density polypropylene (HDPE) were blended with 2% by weight EVOH to determine if the polyolefin type had an effect on regrind stability. Results are shown in **Fig. 5.**

**9.** The effect of EVOH content on thermal stability of regrind




**10.** The effect of $TiO_2$ on PP/EVOH blends (R/PP9 is the actual regrind from PP/tie layer/EVOH product, with EVOH = 3%.)




Both blends of LDPE and HDPE with 2% EVOH did not cause gel formation or screw buildup. Only the PP blend exhibited poor film appearance. Polypropylene is clearly the most common structural resin coextruded with EVOH. Therefore, 10 additional commercially available PP grades from various manufacturers were blended with 0.5% by weight EVOH. The results of this test are given in **Fig. 6.**

Test data indicate that different grades of PP can react differently with EVOH. Only grades PP4 and PP9 had minimal interaction with EVOH. PP5 had high gel levels but did not cause degraded polymer to collect on the screw. All other PP grades reacted unfavorably with the EVOH. Further analysis was conducted with $TiCl_3$, a common catalyst found in virtually all commercial grades of polypropylene. A small amount of $TiCl_3$ was added to EVOH, and the change in melt flow index was monitored over time. This change was compared to the monitored change in EVOH without any additives, and the results are shown in **Fig. 7.**

The EVOH containing $TiCl_3$ experienced a rapid decrease in melt flow index relative to the PP and the EVOH without $TiCl_3$. A chemical reaction can occur between EVOH and $TiCl_3$ from PP, causing EVOH to crosslink. Means to minimize the occurrence of this reaction are to minimize the amounts of $TiCl_3$ and $H_2O$ in the regrind stream. Keeping the melt temperature of the regrind at a minimum is desirable. If feasible, a nitrogen purge on the regrind extruder will also serve to minimize the amount of oxygen in the extruder.

### Effect of EVOH concentration

Blends of PP/EVOH with EVOH concentrations varying from 0.5% to 12% by weight were prepared and tested for thermal stability. PP1 was the PP used as a control, though we had determined that its thermal stability with EVOH was quite poor.

**Figure 8** is the plot of the occurrence of gels in the film over time. Surprisingly, Blends A and B, which have the lower EVOH concentrations, exhibit a higher frequency of gels than Blends C and D. Throughout the 60-min interval, Blends C and D exhibited about 10 gels/100 $cm^2$, which is far less than that of Blends A and B. The qualitative evaluation is given in **Fig. 9.** Gel levels decreased as EVOH concentration increased, though even at 12% EVOH, the film was judged to be rather poor (grade = D). Test data show that gels and screw buildup can occur regardless of EVOH concentration.

### Effect of white masterbatch ($TiO_2$)

White masterbatch ($TiO_2$) is the most common color concentrate used in PP/EVOH coextrusions, particularly in thermoformed barrier trays, cups, and bowls. The presence of $TiO_2$ in multilayer regrind and its effect on thermal stability was evaluated by preparing PP/EVOH using PP9. Though PP9 was not the control PP resin, it was selected because best results were obtained using it in earlier blend studies (Fig. 6). As an additional test, 30% of a PP/tie layer/EVOH regrind was evaluated without adding EVOH. Net EVOH content was 3% by weight. Results are given in **Fig. 10.**

Addition of 4% by weight $TiO_2$ masterbatch to PP/EVOH could cause gels and buildup on the screw even if PP9 is used.

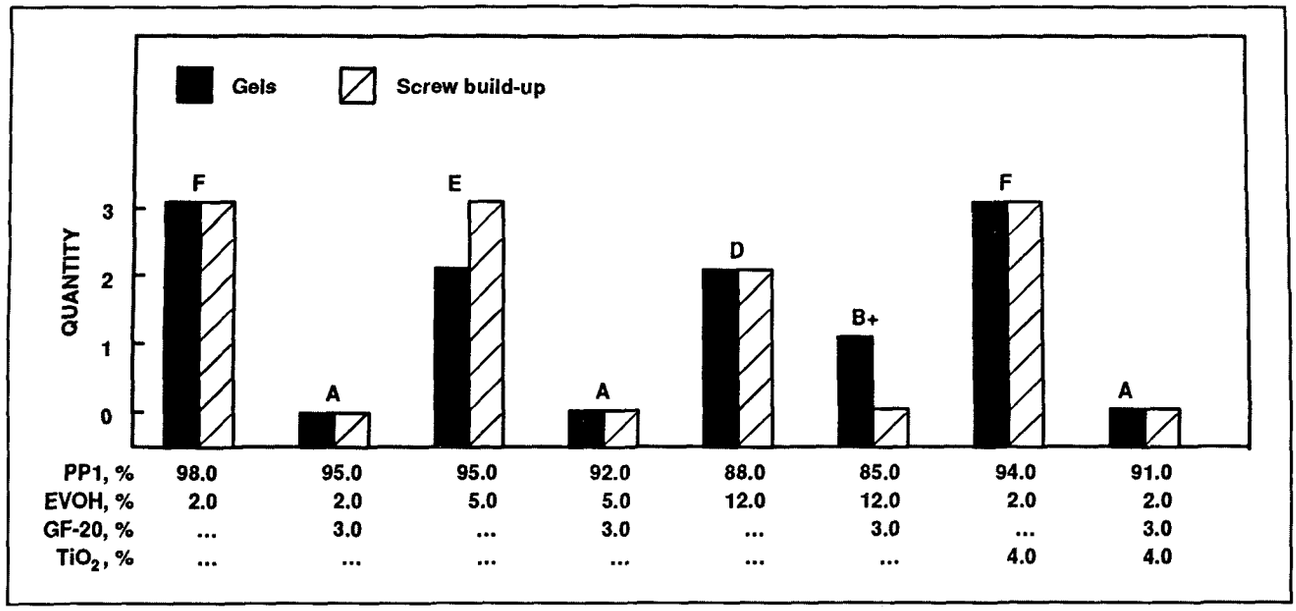
### Effect of using stabilizer masterbatch

Eliminating the use of $TiO_2$ masterbatch and searching for a PP resin without any $TiCl_3$ is not a solution to the apparent problems presented here. $TiO_2$ is a cost-effective and practical colorant. Manufacturing PP without $TiCl_3$ would be a virtual impossibility. Having a knowledge of the various components in the regrind system that have a detrimental effect on its thermal stability is essential to taking the proper corrective action.

A process stabilizer was added to various blends of PP1 and EVOH. $TiO_2$ masterbatch was also included in the evaluation. **Figure 11** shows the results.

A 3% by weight loading of stabilizer masterbatch was

**11.** The effect of using stabilizer $TiO_2$ masterbatch in PP/EVOH regrind (GF-20 is a special regrind stabilizer available from EVAL Co.)




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| PP1, % | 98.0 | 95.0 | 95.0 | 92.0 | 88.0 | 85.0 | 94.0 | 91.0 |
| EVOH, % | 2.0 | 2.0 | 5.0 | 5.0 | 12.0 | 12.0 | 2.0 | 2.0 |
| GF-20, % | ... | 3.0 | ... | 3.0 | ... | 3.0 | ... | 3.0 |
| $TiO_2$, % | ... | ... | ... | ... | ... | ... | 4.0 | 4.0 |

effective in eliminating regrind degradation, the evidence for which is a reduction of gels and screw buildup. The amount of stabilizer masterbatch required can vary, depending on the amount of $TiO_2$ and grade of PP used. Additionally, equipment and processing conditions can affect the amount of stabilizer masterbatch required.

### Processing conditions

Selecting the proper processing conditions is critical in ensuring successful re-use of EVOH-based regrind. In a common sense approach, processing variables should be selected to minimize thermal degradation of the regrind. The melt temperature should be kept to a minimum. In the case of PP/EVOH systems, a good starting point is to target the regrind melt temperature for the same as that used for the virgin PP. Melt temperatures for PP/EVOH regrind systems are typically 220-230°C.

Establishing a consistent homogeneous regrind melt is also important. The most critical variable in achieving a homogeneous regrind melt is the size distribution of the regrind chip. A broad distribution of chip sizes will cause inconsistent extruder feeding and melting characteristics of the regrind.

The single most important factor in processing EVOH-based regrind is using dry regrind. Regrind should always be dried if it is not used within 24 h after grinding. Commonly, regrind is not used immediately after grinding during startup, shutdown, and production interruptions. Every effort should be made to use this regrind within 24 h, or it will absorb water from the atmosphere and will cause sheet bubbling and flow instability ("ocean waves"). If regrind has to be stored for some time, adequate drying can be achieved by using a standard desiccant dryer for a few hours at 90-100°C. Drying of regrind is usually not required when the regrind is processed in a closed-loop system.

### Equipment considerations

Regrind processing equipment can have a great effect on the ability to utilize EVOH-based regrind. Extruder manufacturers are advancing the technology of EVOH regrind use, and the manufacturers are the recommended source of information in this area. For existing coextrusion systems, satisfactory regrind usage can be achieved by using a standard PP extruder (for PP/EVOH) having a length-to-diameter ratio of at least 24:1. Special coatings of melt paths are not needed to process EVOH or regrind that contains EVOH.

## Conclusions

A number of conclusions can be drawn:

1. Regrind containing EVOH can be reclaimed and used in the barrier structure in commercial manufacturing processes.
2. Maintaining the thermal stability of EVOH-based regrind is necessary to maximize the amount of regrind used in the barrier structure. Stabilizer masterbatches can dramatically improve the thermal stability of EVOH-based regrind.
3. The thermal stability of PP/EVOH regrind can be decreased by PP catalyst residues and $TiO_2$ masterbatch.
4. After prolonged storage times, regrind must be dried before use.□

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