TECHNICAL BULLETIN: MIXING PROCESS

POLINTER

1 Introduction

In the manufacture of polyethylene films, it is impossible not considering the use of blends (immiscible mixtures) to obtain final products. For example, the current use of LLDPE would not have a deep impact on film properties if it is not blended with LDPE at different percentages. In the design of multi-layer structures, either by lamination or co-extrusion, it is usual to perform mixing in each layer. Even in low-value added product manufacturing (trash bags or t-shirt bags), the incorporation of regrind or recycled material indicates the presence of more than one component.

However, the preparation of blends tends to be one of the less attractive processes to manufacturers. In many cases, there is no a proper mixing device (or at worst, this is done manually) and rarely the transformer asks to himself (and answers) these questions: *Which is the suitable ratio to reduce costs and, at the same time, maintain product´s properties demanded by customers? Are surface-finish and gel problems caused by the mixing? Am I adding too much recycled material? Is there any particular effect in mixing grinded flakes with pellets?*

The purpose of this guide is to provide the basis to explain in a simple way how a proper blend works, as well as the "to do" and "not to do" list in a mixing process. At the end of this bulletin (references section), there is a list of textbooks and articles wherein these topics are deeply enlightened.

2 Miscible and immiscible mixtures

There are two types of blends: miscible and immiscible. The first one occurs when components disintegrate each other in a way that it is hard to differentiate the components. A common example is water and salt. If a little bit of salt is added in water and is stirred, salt dissolves in, and the water (apparently) remains unchanged. A high-power microscope would be needed to observe both components. On the other hand, an immiscible mixture contains two (or more) phases which are not dispersed. A classical example is water and oil. It does not matter how much this blend is stirred or the temperature at which the mixture is made, eventually, oil will float over the water. It could be questioned that an immiscible mixture be considered as a mixture as well. Figure 1 shows another example of an immiscible mixture (blend): high-impact polystyrene (or HIPS). In this case, a polystyrene (PS) resin with a rubber compound blend is made in order to overcome the high brittleness of pure PS. However, in the photography is shown that rubber phase is not finely dispersed in PS matrix, as supposedly should happen in a miscible mixture. Why is it so useful then? The answer also clears out the paradox of an "immiscible mixture". *Compatible mixtures* have a homogeneous appearance, despite being immiscible, and perform according to their requirements. The aforementioned case of HIPS is an example.

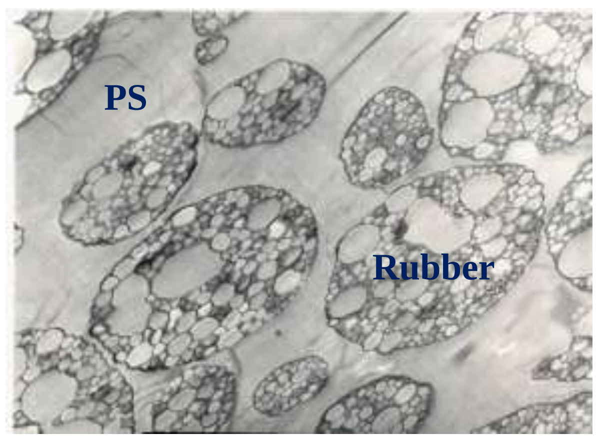

Figure 1. HIPS Under Microscope.

Polyethylene (PE) blends are compatible mixtures examples. PE blends are immiscible, but are compatible through extrusion processing. The reason why a blend of two PE resins (chemically related materials) is not miscible goes beyond the scope of this bulletin, although the explanation can be easily found in many textbooks.[1]

[1] Basically, it is due to Gibbs free energy is positive. More details please see **Torres A.** and **Guastaferro F.** *Mezclas de Polímeros*, Indesca (2005).

3 Dispersive and Distributive Mixing

In so far, we have spoken about mixtures; but… What is mixing? According to the dictionary, mixing is "*joining, put together, incorporate one thing to another*" In a more precise way, it is *"a process to reduce the non-uniformity of composition"* This raises the question *How much non-uniformity is enough?* Unfortunately, there is no a single response, except the statement "enough to achieve consistent desired results", which is not very helpful when defining mixture conditions.

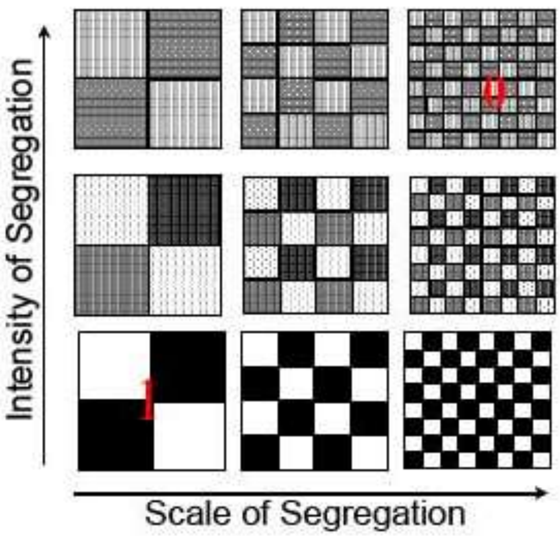

Figure 2. Intensity and scale of segregation.

How does the components uniformity of a mixture break? Let's suppose we have two large cubes of material, a white cube and a black cube that we want to mix in order to obtain a grey cube. The first approach is to start breaking the large cubes into smaller pieces, and arrange them alternately (Step 1 of Figure 2).[2] If this continues, mixing would only move horizontally, making smaller cubes, ***distributing*** each component in a more uniform pattern, but without equal concentration of components in any other part of the mixture (as a matter of fact, any zone could contain 100% of one component and 0% of the other one). Therefore, it is necessary to ***disperse*** a component into the other, or move vertically along the axis of Figure 2. As in the previous case, if mixing is only dispersive, it is possible to reach the same concentration in all cubes, but these pieces would maintain their original size. An ideal mixture requires distributing the components, as well as dispersing original sizes in order to achieve the ideal condition (upper right "0" in Figure 2).

The above mentioned, describes two types of mixing process that must be kept in balance to ensure an efficient mixture (and to implement in an economical way): ***dispersive mixing process*** (or rupture of mixture components into very small pieces), and ***distributive mixing process*** (a homogenous distribution of mixture phases). In Figure 3 the dispersion and distribution of a minor component (red) into a major component (green) are shown. This is applying both mixing mechanisms. On the top, a purely dispersive mixing process is shown, where particles are broken and still remain undistributed, followed by a distributive mixing process as final step. At the bottom, the sequence is altered, just to get always similar results. These processes occur simultaneously so it is **impossible** to separate the distributive mixing from the dispersive mixing, and vice versa. Mixing equipments will work in one way or another, but there are no purely distributive or dispersive mixing equipments.

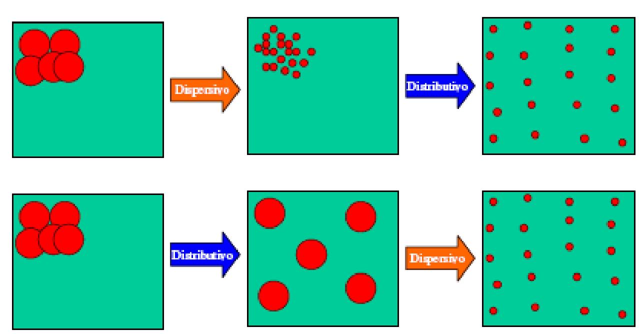

Figure 3.Differences between dispersive and distributive mixing (the sequence of mixing processes does not affect the final product).

[2] A more detailed and technical explanation can be found at **Manas-Zloczower**, **D.** And **Tadmor Z.** *Mixing and Compounding of Polymers: Theory and Practice.* Hanser, Munich, Germany (1994), and in **Uhl V.** And **Gray J.** *Mixing: Theory and Practice.* Academic Press Inc. San Diego, USA, 1967.

Extrusion screws are designed including dispersive and distributive mixing elements in an effort to improve the mixing capacity. In fact, the standard screw design is performed in order to produce both mechanisms. The dispersion occurs when material passes through the screw flight clearance. Since the space between the screw flight and the barrel is narrow, a pellet or grain passing through this gap would break. Into the screw channel, are generated vortex flow patterns, which promote the distributive mixing.

However, these mechanisms frequently are insufficient to guarantee a good mixing. Therefore, screw geometries usually include elements designed for dispersive and distributive mixing. Examples of those elements are shown in Figure 4.

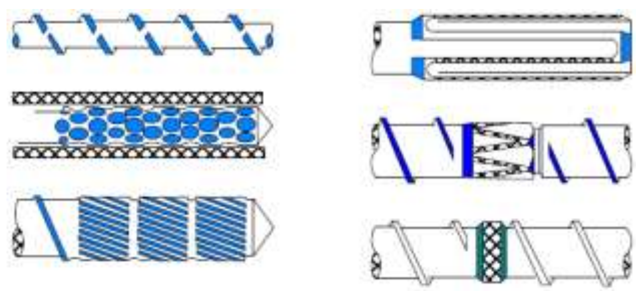

Figure 4. Distributive (left) and dispersive (right) mixing elements normally used in extruders with PE.

Distributive mixing elements are characterized by having irregular or discontinuous sections which break the pre-established flow pattern, generating vortices or swirls of the material and establishing more or less chaotic flow regimes, ideal for homogenizing the mixture[3]. These elements are usually located at the end of the screw, since the mixture is supposed to be finally dispersed (in fact, the solid elements should have already been melted). On the other hand, the *dispersive mixing elements* generally consist of flow restrictions in order to "break" any agglomerate whose size hinders the passage through the restriction. These elements are located before the distributive mixing elements. A dispersive mixing element will cause a relevant increase in power consumption and melt temperature, while the distributive mixing elements induce marginal increases.

Finally, it is important to point out that there is no mixing element which is purely dispersive or purely distributive. Any of the elements shown in Figure 4 produces dispersive mixing and distributive mixing, in a greater or lesser degree. The classification derived from elements incorporated to screw geometry considers the preferred type of mixing that these elements perform.

4 Factors to consider when making a mixture.

Many of the important factors that determine the difference between a "good" or "bad" mixture have already been outlined in previous theoretical sections. Utracki[4] proposes a checking list which is recommended to be followed when defining a mixture:

- **Define the mixture's desired properties in a quantitative form:** set clearly what you want to get from the mixture: better tear resistance, less haze (cloudiness), good balance between mechanical properties and processability. Try, as much as possible, to set specific values for target properties. Your resin supplier can help you with this assessment.

- **Select candidate resins according to the desired properties:** there are a lot of resins available. Each supplier will surely be able to offer more than one option to meet the mixture requirements. Besides prices, it is important to know in detail resins properties.

- **Tabulate the pros and cons of each resin. This will allow alternatives identification:** keep in mind that some grades are differentiated only by the types of additives and

[3] An analogy which allows an easy comprehension of why this type of geometry is chosen is the egg beating. The egg yolk dissolves much easier and with less effort than white using a fork instead of a spoon. The fork breaks the circular flow pattern imposed by hand movement, generating not only circular movement, but rectilinear movements between the fork tines is also created.

[4] **Utracki, L.** Polymer Alloys and Blends: thermodynamics and rheology. Hanser Munich, Germany. 1989

their content. Resin suppliers offer a wide range of products,from high viscosity resins (lower processability and good mechanical properties) to low viscosity resins with lower mechanical properties and excellent processability. Also consider variation in density. As a rule, you should try to find similar MFI resins (MFI=Melt Flow Index is usually one of the two properties already known at the beginning of the project). Again, your resin supplier and its technological partner are the best support in choosing an appropriate resins combination.

- **Select resins with the best potential for fulfilling mixture requirements:** this potential should be defined as first point of this list.

- **Determine the miscibility of resins or provide the means to make them compatible:** sometimes, ideal products require compatibilizers or special processing conditions. Verify your capabilities to obtain these conditions ensuring that additives do not excessively increase the formulation cost or affect key properties.

- **Make a first cost estimate:** if the scenario looks attractive, go ahead; otherwise, choose another set of resins (step 4).

- **Analyze the mixture selected from processing and final application perspective:**
  - ✓ Is it obvious that this is going to work or not?
  - ✓ Could it be processed with the available equipment?
  - ✓ Will it keep its properties throughout its useful life?

It is always advisable to prepare a small lot. Analyze it deeply, and compare it to an existing product (the one you wish to match). If this analysis indicates that the product is successful, then it should be tested with a trusted client, warning that it is an experimental product. It is important to be open to criticism and customer recommendations to check proportions, components and processing conditions. In technical projects, the first step is the most difficult; as development cycle is overcome, time and resources decrease. It is just important to document **all** of the steps taken. The information related to a failed stage in the process could be the solution to another need. Is not perhaps the history of mankind full of discoveries by accident or development of a product looking for another?

5 Mechanical mixing, melt flow mixing, or both?

Once the mix is "approved", it is time to manufacture it formally. The initial mixing for testing could have been done even in facilities other than the manufacturer (R&D facilities, resin supplier, pigments or additives suppliers), followed by the decision of selecting the most appropriate mixing process: mechanical or melt flow mixing.

Obviously, when passing through the extruder it will be performing a melt flow mixing. Now, if you want to use the extruder as a mixer, be sure that it is properly configured to run this function. Even though all extruder is a mixer, it is important to guarantee that there is at least one distributive mixing zone and, preferably, a dispersive mixing one. Concerning any improvement in mixture quality, it is advisable to make a previous run through an extruder.

Regarding mechanical mixing process, the most important thing is to have equipment that allows a good distributive mixing, since dispersive mixing is minimal. Commercially, there are many mixing equipments available that range from rotating drums up to very sophisticated mixing equipments (see examples in Figure 5).

All of these equipments operate under the same principle: a circular motion (rotation) with a transverse motion perpendicular to the first one, in order to shake the mixture vigorously, encouraging the distributive mixing. Also note that those more complex models try to break the symmetry of the container, just to establish non-uniform flow patterns.

Mixers should be used partially empty in order to guarantee free movement of mixture components. It is recommended to fill them up to 2/3 of capacity just to get a balanced volume- mixing capacity ratio.

(a)

(b)

(c)

(d)

Figure 5. Commercial mixer examples.

a) Drum with inner palettes.

b) Rotating drum.

c) Twin mixers.

d) Double-cone mixer.

Finally, any manual mixing should be discarded at once: shaking of bags, manual agitation of products in a drum, stir a bag with a stick. The inefficiency, lack of repeatability, and inappropriate mixing will promote high variation in product quality.

Figure 6. Feed hopper mixers.

If high volumes will be mixed, it is required an uniform mixing; when liquids, powders and/or pellets are going to be used, it is recommended using feed hoppers mixers in line, as shown in Figure 6. These devices have a large mixing capacity which provides excellent mixtures, but also consume a lot of energy and their cost is higher than the rest of the options mentioned in this bulletin.

6 Synergy and antagonism. Final product properties

Knowing the complexities of mixture manufacturing, a further difficulty appears: What properties will the mixture have? It is required to measure all the product's key properties, but transformers would like to handle tools to predict the final product performance.

Normally, an uninformed reader would say that final properties will be in proportion to the original component's property multiplied by its concentration. This is true, if two products are mixed: a two components mixture is made at 50% each, one with a property value of 30, and the other with a value of 60, the mixture´s final property should be 45 (from 45=30·50% + 60·50%).

This principle is generally known as the law of mixtures. However, the same does not occur in immiscible mixtures, such as polyethylene blends, and it is only expected in miscible mixtures. In most cases **synergy** (the mixture´s property is greater than expected from the law of mixtures) or **antagonism** (the mixture´s property is lower than expected from the law of mixtures) phenomenon are produced. This is graphically shown in Figure 7, where the dotted line indicates the expected behavior based on the law of mixtures. The solid line and red boxes indicate the actual behavior and the tests performed, respectively. It can be seen in the middle of graphic line (50% or 1:1 components ratio), the mixture performance is the worst possible. This happens due to this polyethylene blend shows antagonism. On the other hand, in cases where one component concentration is dominant (right zone or left zone from middle point), the blend performance is better than expected according to this law. In these ranges the blend is synergic.

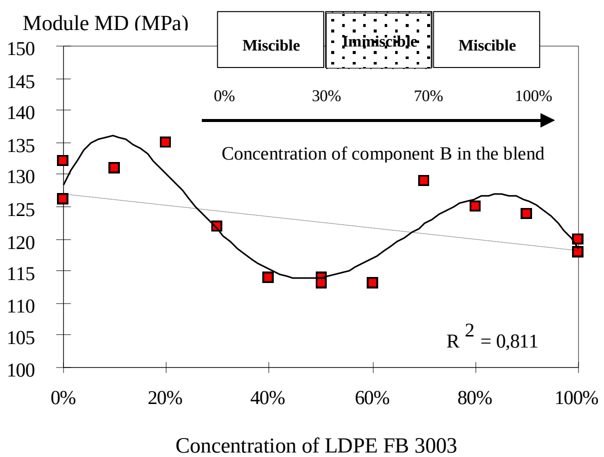

Figure 7. Elastic module as a function of LDPE Venelene® FB3003 concentration in LDPE Venelene® 11F1 blend.

The above example is true for almost any polyethylene blend. The 50-50% mixing area should be avoided as much as possible. This mixing is a two immiscible phases mixture, neither of them is "dominant", alternating weakly linked regions of materials are present into it. When one phase is dominant, incorporations of minor component groups into the major one are produced (as shown in Figure 1), forming synergistic alloys with better final product's properties (mechanical, physical, optical), and optimum material processability (see Figure 8).

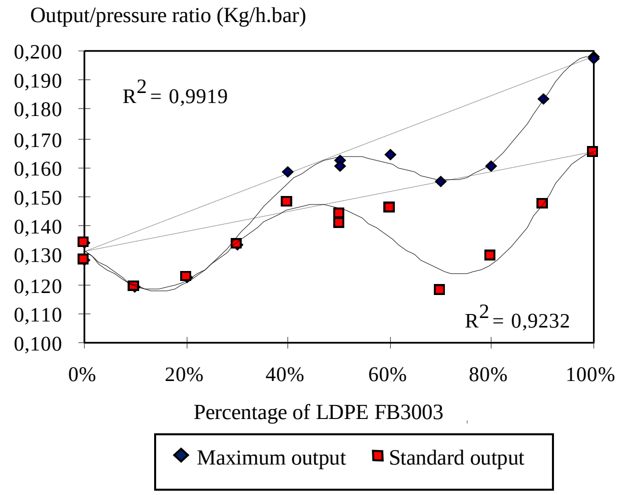

Figure 8. Effect of LDPE Venelene® FB3003 content when processing LDPE Venelene® 11F1.

7 Use of recycled material

The use of recycled, recovered or regrind material could have two opposite effects: costs are reduced in a very simple manner, and a relatively good quality compound is obtained. For automatic as well as heat shrinkable packaging, and for almost all film production processes, the manufacturer faces a hard competition in a business with very small profit margins. In consequence the most efficient manufacturer with lower costs is able to maintain a healthy financial business situation. Therefore, the temptation to add a bit more than necessary of regrind material is very strong.

Regardless final product properties and keeping focus on the mixing process, you should be aware that these products must be grinded and prepared before being added back to the extruder. It is very difficult to obtain a particle size similar to pellet resin provided by suppliers. In most cases, flakes or small cylinders – like material will be obtained. When feeding the extruder, a segregation phase may be produced, especially in the feeding throat caused by differences in shape. This will prevent an appropriate mixing process, causing failures on appearance (gels, strands), defects in optical properties, poor mechanical properties (low tear resistance, low puncture and impact resistance), and in extreme conditions, a collapse of production line.

It is impossible to consider an appropriate range of recycled material concentration to be added into the virgin material. Only through systematic measurement of properties (not only of the final product, but also of the process) will determine the proper concentration level. Obviously, mixing process must be more intensive as the proportion of recycled material increases, whose shape differs from the standard pellets shape.

8 Summary

For many reasons, there is a tendency to pay little attention to the mixing process, which is present in many plastics manufacturing processes. Nevertheless, in a competitive market, the difference between a successful product and one unsuccessful, often lies on the appropriate components selection and its concentrations, the use of adequate mixing equipments and the understanding of the mixture compatibility areas. This bulletin brings a basic guide to introduce readers to ask themselves questions whose answers will allow the improvement of their company's performance.

As a summary, the following should be kept in mind:

- ⇑ The mixing comprises two mechanisms: **the dispersive mixing process** (splitting the elements into smaller-sized components) and **distributive mixing process** (homogenization of the relative presence of two components in the entire mixture).
- ⇑ The extrusion screw with standard geometry configuration is a good dispersive mixing tool. However, the incorporation of dispersive elements is recommended for many plastics process.
- ⇑ Polyethylene blends do not follow the law of mixtures. They can show **synergy** or **antagonism**, depending on the materials to be mixed and their proportions. It is preferable to have a synergistic blend.
- ⇑ The lowest possible difference in viscosity should be maintained between the materials to be mixed.
- ⇑ It is **extremely important** to document as much detailed as possible, the steps, successes and failures in the development of a mixture. Keep in mind that the world is full of successful inventions that were achieved while searching something different.
- ⇑ A full filled mixer is not efficient. Fill up to 70% of the mixer capacity.
- ⇑ Polyethylene blends are immiscible, but compatible.
- ⇑ The 50% - 50% mixing region should be avoided. A major proportion should always be kept (at least 60%).
- ⇑ Excessive recycled, regrind or post-industrial material use should be avoided. Besides the expected loss of properties, the after-cutting shape of these materials is very different from the virgin resin pellets, which could cause segregation problems in the extruder feeding area.

9 References.

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In order to obtain more detailed information of the security aspects regarding the use and disposal of our products, we invite you to consult the material safety data sheets (MSDS) for Venelene® polyethylene.