

TECHNICAL BULLETIN: MIXING PROCESS



1 Introduction

In the manufacture of polyethylene films, is almost impossible not considering the use of mixtures to obtain final products. For example, the current use of PELBD would not be too shocking if wasn't mixed with several percentages of PEBD. Even in the design of multi-layer structures, either by layering or co-extrusion, it is usually considered mixtures in each layer. Even in the manufacture of low added value items (trash bags or t-shirt bags), the incorporation grinded or recycled material indicates the presence of more than one component.

However, the elaboration of the mixtures tends to be one of the aspects that do not attract the attention of manufacturers. In many cases, there is not a proper mixing device (or in the worst of the cases, this is done manually) and in seldom times the transformer questions (and answers) these questions: *Which is the suitable ratio to reduce costs and maintain the properties demanded by my customers? Appearance and Gel problems are caused due to the mixes I am doing? Am I adding too much recycled material? Is there any particular effect to mix the grinded flakes with pellets?*

The purpose of this guide is to provide the basis to explain in simple terms how a proper mix works, as well as the dos and don'ts. In the references at the end of the article, there is a list of textbooks and articles wherein these topics are deepened.

2 Miscible and immiscible mixtures

There are two types of mixtures: miscible and immiscible. The first occurs when components spread each other such it's hard to differentiate the components. A common example is water and salt. If a little salt is added in water and is stirred, salt dissolves in water and (apparently) remains unchanged, even if you cannot drink it because it's salty! A high-power microscope would be needed to see both components. On the other hand, an immiscible mixture is that in which both (or more) phases are not spread. A classical example is water and oil. It does not matter on how much are stirred or the temperature in which the mixture is made. Eventually, oil will float on the water. It could be questioned that a mixture is not immiscible as such. Figure 1 shows another example of an immiscible mixture: High-impact polystyrene (or PSAI). In this

case, a Polystyrene (PS) mixture with rubber is made in order to overcome the high fragility of PS in its pure state. However, in the photography is seen that rubber is not finely spread in PS, 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. Mixtures that, even if appear to have a homogeneous effects, and behave pursuant its purpose are called compatible. The aforementioned case of PSAI is an example.

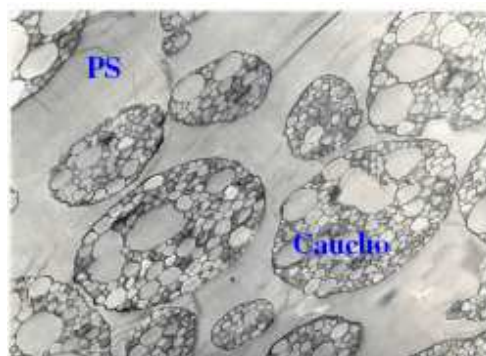


Figure 1. PSAI under Microscope

Polyethylene (PE) mixtures are other case of compatible mixtures. PE mixtures are immiscible, but are compatible through extrusion processing. The reasons why a mixture of two types of PE of similar materials at the beginning is not miscible are beyond the scope of this bulletin, although the explanation can be easily found in any text¹.

3 Dispersive and Distributive Mixtures

In so far, we have spoken about mixtures; but... What is a Mixture? According to the dictionary, to mix is "join, merge, incorporate, an item with another" This raises the question *How much uniformity is enough?* Unfortunately, there is not a single response, except the one that states that "Enough to achieve consistent desired results",

¹ Basically, it is due that the Gibbs free energy is positive. Form more details, please see **Torres A. And Guastaferrero F. Mezclas de Polímeros**, Indesca (2005)

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which is not very helpful when defining mixture conditions.

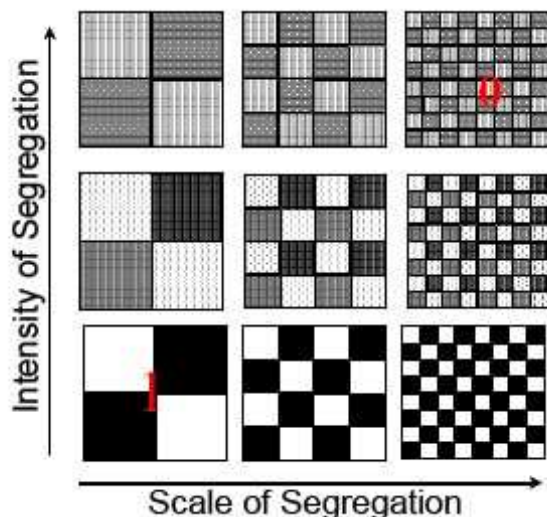


Figure 2. Intensity and Scale of Segregation

How is broken the uniformity of the components of a mixture? Let's suppose that we have two large cubes of material, one white and one black that we want to mix in order to obtain a grey cube. The first comprises on turn the cube into two parts and place them in an alternate way (Step 1 of Figure 2)². If we continue doing this only, the mixer would only move horizontally, making smaller cubes, **distributing** each component in a more uniform mode, but without the same concentration of the components in any other part of the mixture (as a matter of fact, in any zone there would be 100% of a 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 the mixture is only dispersed, it is possible to reach the same concentration in all cubes, but these would have the initial size. If the process would be endless in time, we would reach a perfect mixture following only the horizontal or the vertical paths, but the reality is other! Actually, it is required to distribute the

components, as well as disperse their initial sizes in order to achieve the suitable stage ("0" in Figure 2).

The aforementioned takes us to two kinds of mixtures to keep in its fair balance in order to guarantee the efficiency of a mixture (in an economical way) **dispersive mixture** (or rupture into very small components of the mixture), and **distributive mixture** (a homogenous distribution of the phases of a mixture). In Figure 3 it is graphically shown the dispersion and distribution of a minor component (red) into a major component (green), following both mixture mechanisms. In the superior part it is seen that if it is applied first a purely disperse mixture, particles will be broken, but will remain undistributed; as this happens in the following step. In the inferior part, the order is altered, with the same results always. Both situations are suitable as it is **impossible** to separate the distributive mixture from the dispersive and vice versa. Mixture equipments will preferably do either one function or another, but there are no purely distributive or dispersive mixture equipments.

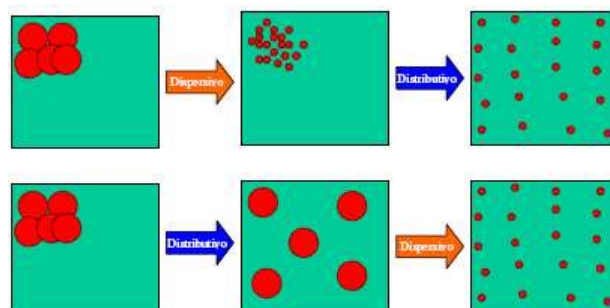


Figure 3. Differences between dispersive and distributive mixtures. Note that the order of mixing processes does not affect the final product.

The extrusion screws are designed so that they possess dispersive and distributive elements. In fact, the general design of the screw is made in order to produce both mechanisms. The dispersion happens when the material passes through the screw fillets; since the space between the fillet and the barrel is very small, a pellet or grain of dust passing through fillet-barrel space would cause it to

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.

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break. Flow patterns with vortices which favor the distributive mixture are produced in the duct.

However, in many occasions these mechanisms are insufficient to guarantee a good mixture. This is why the screws usually have elements specifically designed for the dispersive and distributive mixtures, respectively (keeping in mind that neither performs exclusively the dispersive or distributive mixture, respectively). Examples of these elements are shown in Figure 4.

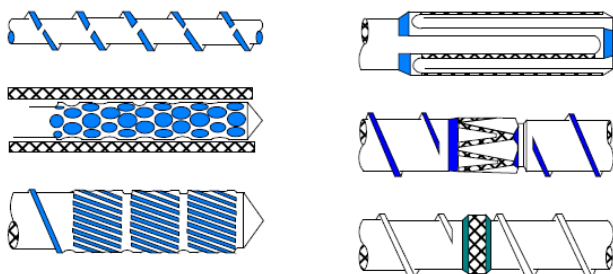


Figure 4. Distributive (left) and dispersive (right) elements normally used in extruders with PE.

Note that the distributive 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 mixture³. These elements are usually placed 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 elements generally consist of flow restrictions in order to “break” any agglomerate whose size hinders the passage through the restriction. These are placed before the distributive elements. A dispersive element will cause a relevant increase in the power consumption and casting temperature, while in the distributive elements, this increase is, at worst, marginal.

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

Lastly, it is important to point out that there is no element which is purely dispersive or purely distributive. Any one of the elements shown in Figure 4 generates both mixtures, in a greater or lower grade. The classification arises from taking into account the type of preferred mixture that a determined element performs.

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 a theoretical manner in the previous sections. Utracki⁴ makes a checking list which is recommended to be followed when defining a mixture:

- **Define the desired properties for the mixture in a quantitative form:** clearly establish what you desire to obtain from the mixture: better tear, less cloudiness, balance between mechanical properties and processability. Try, as much as possible, to establish specific values of the target properties. Your resin supplier can help you with this assessment.
- **Select the candidate resins according to the desired properties:** there are endless numbers of resins available. Each supplier will surely be able to offer more than one in order to reach the purpose of the mixture. Besides the price, it is important to know in detail each of their properties.
- **Tabulate the pros and cons of each resin. This will allow the identification of alternatives:** keep in mind that some grades differ only by the additives package present. Resin suppliers offer a range of products that go from the ones with high viscosity, lower processability but good mechanical properties, up to the ones with low viscosity with lower mechanical properties but excellent processability. Others also vary in density. As a rule, you should try to find those which IF

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

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differences (usually one of the two only properties that are already known at the beginning of the project) are as few as possible. Again, your resin supplier and his technological allies are the best help in choosing an appropriate materials combination.

- **Select resins that, according to the previous step, show the best potential for fulfilling the mixture requirements:** this potential should be defined in point 1 of this list.
- **Determine the miscibility of resins or establish the means to make them compatible:** sometimes, ideal products require a compatibility agent or special processing conditions. Verify that you are able to meet these conditions and that the agents do not excessively increase the formulation or affect the key properties.
- **Make a rough cost estimate:** If the numbers seem appealing, proceed; otherwise, choose another resin set (step 4).
- **Analyze the selected mixture from the processing and final application point of view:**
 - ✓ Is it obvious that this is going to work or not?
 - ✓ Can 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 in depth, and compare it to the existing product or to the competitor whom you wish to match. If this analysis indicates that the product is successful, you should then try it with a trusted client, warning him that it is an experimental product. It is important to keep an open mind to criticism and suggestions from the client in order to check proportions, components and processing conditions. As in all technical projects, the first steps are the most difficult, as the development cycles are made, the necessary time and resources decrease. It is just as important to document **all** of the steps taken. The information regarding a failed stage in the process may be the solution to another need.

Isn't human history full of accidental discoveries or developing one product while seeking another?

5 Physical mixture, casting mixture, or both?

Once the mixture is "approved", it is time to formally produce it. The initial mixture for testing could even have been made in different facilities from the producer's (R&D facilities, resin, pigment or additive suppliers), thus reaching the decision whether the product mixture should be physical or by casting.

Obviously, when passing through the extruder you will be performing a cast mixture. Now, if you desire to use the extruder as a mixer, you must make sure that it is configured to properly execute this function. Even though the extruder is more or less a mixer, it is important to guarantee that there is at least one distributive mixing area and, preferably, a dispersive mixing one. Otherwise, it is advisable to consider the mixture quality.

Regarding the physical mixture, the important part is to have equipment that allows a good distributive mixture, due to the fact that the dispersive mixture is minimal. Commercially, there are many mixing equipments available that range from the use of a rotating drum up to very sophisticated mixing equipments (see examples in Figure 6).

Note that all of them operate under the same principle: besides a circular movement, there is also a transverse movement, perpendicular to the circular movement, with the purpose of strongly shaking the mixture, encouraging the distributive mixture. Also note that we attempt to break with the container symmetry in the more complex models so that uniform flow patterns cannot be formed.

The mixers should be used partially empty in order to guarantee the free movement of the mixture components. It is recommended to fill them up to 2/3 of their capacity so that there is a good relation between the volume and the mixing capacity.

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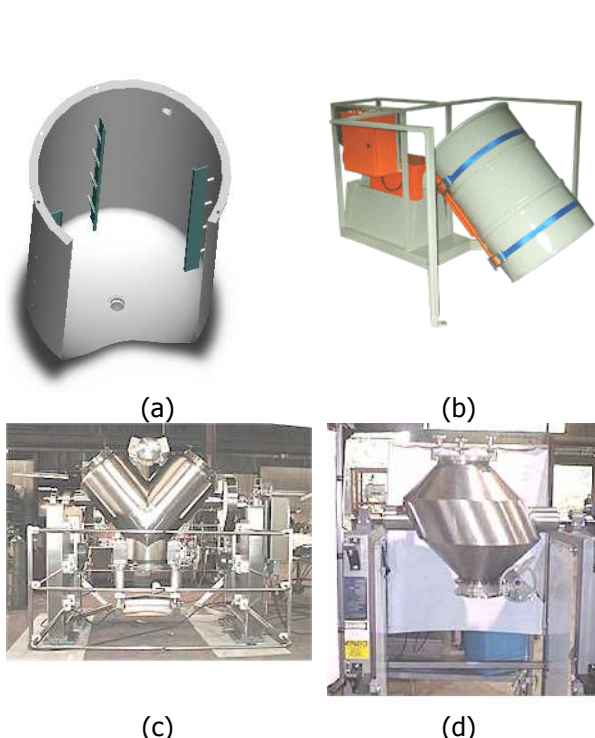


Figure 6. Commercial mixer examples.

- a) Drum with inner palettes.
- b) Rotating drum.
- c) Twin mixer.
- d) Double-cone mixer.

Lastly, any manual mixing should be discarded at once: shaking of the bags, manual agitation of the products in a drum, mixing a bag with a stick. The inefficiency, lack of receptiveness and inappropriate mixing will make an adventure out of each lot.

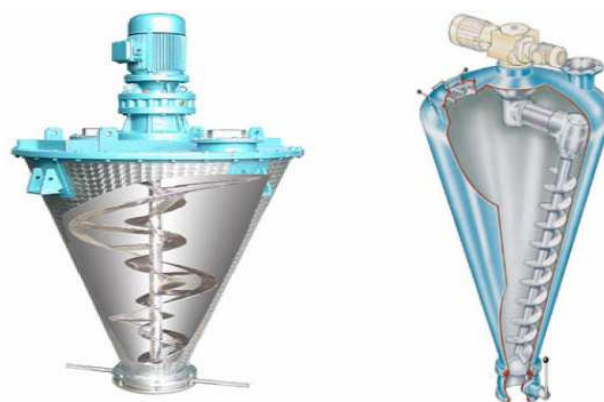


Figure 5. Hopper mixers.

The placement of in line (hopper) mixers, as shown in Figure 5, is recommended in case the volumes to be mixed or produced are very large, or if a more uniform mixture is required, or if liquids, powders and/or pellets are simultaneously used. They have a large mixing capacity which provides excellent mixtures, but also consume a lot of energy and their cost is greater than the rest of the options studied in this bulletin.

6 Synergy and conflict. Final product properties

Having known the complexities of manufacturing the mixture, another difficulty arises: What properties will the mixture have? It is required to measure all the product's key properties, but every transformer would like to have at hand the tools which predict or approximate the answer of the final product.

Normally, an unaware reader would dare say that the final properties will be in proportion to the product of the original component's property multiplied by its concentration. This is true, if two products are mixed: one with a property whose value is 30 with another whose property is 60 and making the mixture at 50%, the property of the mixture should be 45 ($45=30 * 50\% + 60\% * 50\%$).

This principle is generally known as the law of mixtures. However, the same does not occur in immiscible mixtures, such as the case of

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polyethylene mixtures, and it should only be expected in miscible mixtures. In most cases the **synergy** phenomenon is produced (the mixture property is greater than what is expected from the law of mixtures) or **conflict** (the mixture property is lower than what is expected from the law of mixtures). 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 colored boxes indicate the actual behavior and the tests carried out, respectively. It can be seen that in the center of the graphic (at approximately a 1:1 or 50% relation of each component), the mixture performance is the worst possible. This happens due to the fact that the mixture is conflictive. On the other hand, in cases where is major (be it on the right or the left of the Figure), the mixture performance is better than what should be expected according to this law. This occurs because the mixture, in this rank, is synergic.

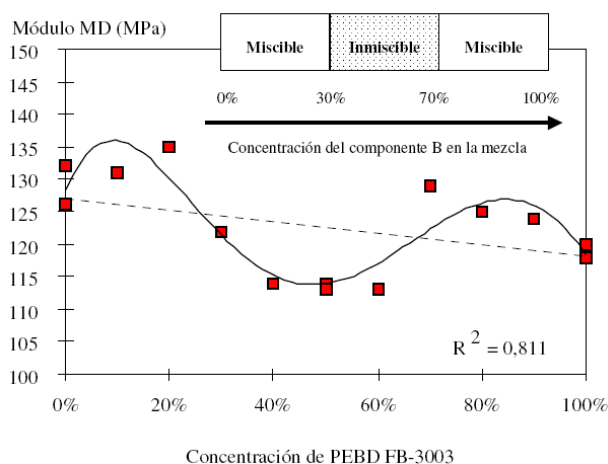


Figure 7. Elastic module in the Venelene® 11F1 PELBD in function of the Venelene® FB3003 PEBD concentration.

The previous is a valid example for almost any polyethylene mixture. The 50-50% mixing area should be avoided as much as possible. The reason lies in, being two immiscible phases, neither of them is "dominant", and alternating areas of a material are produced, followed by or together with (weakly, since they are immiscible) the area of the other material. On the on the contrary, when the phase is dominant, incorporations of minor element

groups are produced in the major element (as shown in Figure 1), forming synergetic alloys that are not limited only to the final product's properties (mechanical, physical, optical), but are also reflected in the material processability (see Figure 8).

7 Use of recycled and recovered material

The use of recycled, recovered or reground material is a double-edged sword: on the one hand, costs are reduced in a very simple manner and, in the case of regrinding, a relatively good quality material, which would otherwise be wasted, is reprocessed. Both in the automatic as well as the heat shrink package, and for almost all of film production processes, the transformer is faced with hard competition in a business which has very small profit margins and where only the most efficient processor with lower costs is able to maintain a healthy financial business situation. Therefore, there is a very strong temptation of adding a little more than what is necessary.

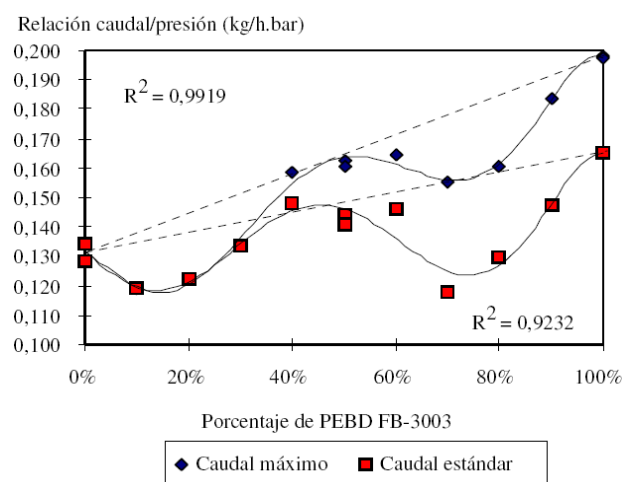


Figure 8. Effect of the Venelene® FB3003 PEBD content when processing the Venelene® 11F1 PELBD.

Without getting into considerations regarding final product properties and only maintaining focus on the mixing process, you should keep in mind that these products must be ground and prepared to be added to the extruder again. It is difficult (to say

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the least) to obtain a particle of similar size to the pellet provided by the resin supplier. In most cases, a flaky or small cylinder –like material will be obtained. When feeding these materials to the extruder, a segregation phase may be produced, especially in the feeding area, product of the difference in shapes. This prevent an appropriate mixture and will very likely cause flaws in appearance (gels, strands), defects in optical properties, flaws in the mechanical properties (especially in the tear, penetration and impact resistance), and, in severe cases, a collapse of the production line.

Given the wide variety of products that can be made by tubular film extrusion, it is impossible to establish a maximum percentage appropriate for post-process component addition. Only the systematic measurement of properties (not only of the final product, but also of the process) will determine said percentage. What does result obvious is that the mixing must be more intensive as the percentage of the material increases whose shape drifts away from the shapes of the pellets.

8 Summary

For many reasons, there is a tendency to pay little attention to the mixing process, which is present in almost all of the tubular film applications. Nevertheless, in the competitive world of blown films, the difference between a successful product and one that isn't, often lies on the appropriate selection of components and concentrations, the use of adequate mixing equipments and the understanding of the mixture compatibility areas. This bulletin is intended to be a basic guide to introduce the reader to ask himself questions whose answers will allow the improvement of his company's performance.

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

- ↑ The mixing comprises two mechanisms: **the dispersive mixture** (splitting the elements into smaller-sized components) and **distributive mixture** (homogenization of the relative presence of both components in the entire mixture).
- ↑ The extrusion screw, in its basic configuration, is a good dispersive mixture element. However,

the incorporation of dispersive elements is recommended for tubular film processing.

- ↑ The polyethylene mixtures do not follow the law of mixtures. Its behavior can be synergetic or conflictive, depending on the materials to be mixed and their proportions. It is preferable to have a synergetic mixture.
- ↑ The lowest possible difference should be kept between the viscosities of the materials to be mixed.
- ↑ It is **extremely important** to document, with the greatest detail 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 seeking something different.
- ↑ A full mixer is inefficient. Maintain the capacity level close to 70%.
- ↑ The extrusion screw, in its original configuration, offers a low distributive mixture. It is advisable to include a distributive mixture element.
- ↑ Polyethylene form immiscible, but compatible, mixtures.
- ↑ Mixing in the 50% - 50% region should be avoided. A major proportion should always be kept (at least 60%).
- ↑ Mixtures with excessive recycled, reground or post-industrial material should be avoided. Apart from the expected property loss, the shape of these materials after cutting is very different from the virgin resin pellets, which could cause segregation problems in the extruder feeding area.

9 References.

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This bulletin has been made by the Marketing Department of Polinter with the support of the specialists of Investigación y Desarrollo, C.A. (INDESCA) and by the Technical Services Department of CORAMER. This is intended for all clients and users of the Venelene® resins and we trust that the information contained herein is helpful and useful.

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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 security pages (MSDS) of the Venelene® Polyethylene.