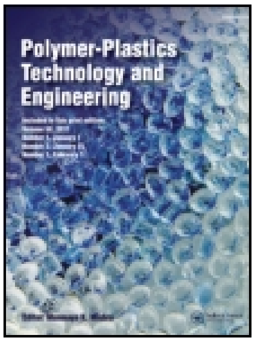

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Morphology Development of Immiscible Quaternary Polyolefin and PS Blends

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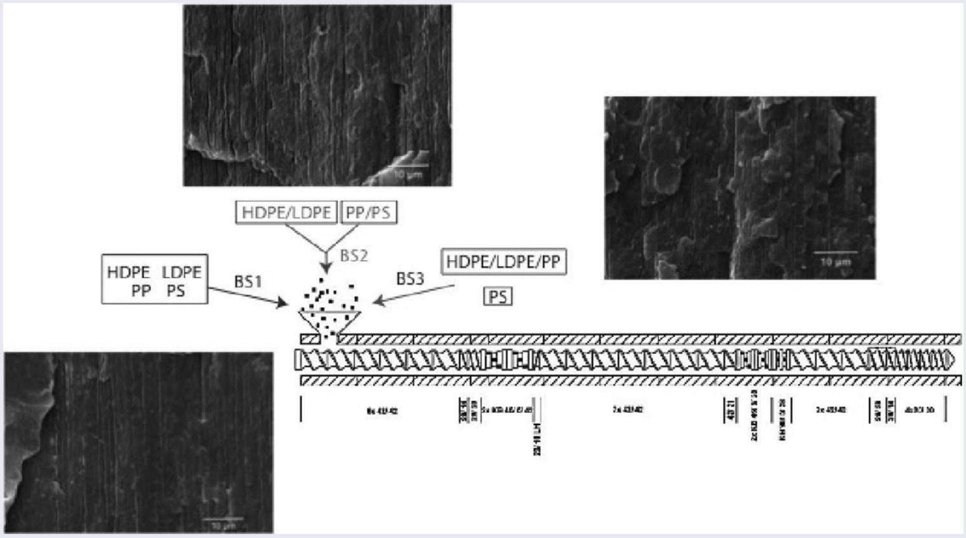
ABSTRACT

Study of polymer blends that fulfill the current engineering demand has been increased in the last years and multicomponent blends are still a challenge, but increasing the number of components will lead to further complications. We correlated the differences between morphology and blending sequence in quaternary blends of polyolefin with polystyrene, following the available theories that related viscosity and morphology. It was found that high viscous matrices enhance deformation and breakup processes, displaying fibrillar morphologies and finer dispersions. The blending sequence improves the mixing first, by putting all the polyolefin into a ternary blend and after that, adding the polystyrene.

KEYWORDS
Blending sequence; immiscible multicomponent blends; particle size analysis; phase morphology; viscosity ratio

GRAPHICAL ABSTRACT



Introduction

Polymer blending, a versatile, effective, and economical practice, is commonly used to obtain materials with customized properties. Blending more than three polymers is a difficult task, especially because it is problematic to predict the morphology and the final properties. How to control the morphology in multicomponent blends continues to be a challenge in spite of the large efforts carried out during the last decade. Besides, polymer rheology is a key point, because it affects the final mechanical properties[1–6].

Regarding polyolefins blends, currently there are efforts to use recycled materials in binary blends[7] or to use compatibilizer agent like Ethylene propylene diene monomer rubber (EPDM)[7,8] or different EP copolymer[9,10]. However, polyolefins are the main components, 60–70% with polystyrene (PS), polyethylene terephtalate (PET) and polyvinyl chloride (PVC) are the main plastics in the landfill. A good practice in terms of environmental and economical reason should be blending several of these materials[11] without any compatibilizer agent.

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Table 1. Basic material characteristics.

Polymer	T_m (°C)	T_g (°C)	MFI (g 10 min^{-1}) 200°C, 2.16 kg	E (MPa)
iPP	167.21	—	6.4	1018.67
HDPE	167.64	—	0.3	882.02
LDPE	133.74	—	2.9	184.06
PS	—	109.97	4.3	1550.86

MFI, melt flow index.

The aim of this work is to study the relationship between morphology and blending sequence in quaternary blends. We apply the available theories for binary blends to predict the morphology and showing an experimental approach between the rheological behavior of the components and the final phase of morphology. Polyolefins like high density polyethylene (HDPE), low density polyethylene (LDPE) and polypropylene (PP) were blended with two different composition of PS in a twin-screw extruder.

PS shows a fibrillar morphology with some differences, because of the blending sequences and composition. However, minor droplet morphology is still present. The morphology obtained is in accordance with the rheological behavior of the polymers.

Experimental

Materials

The polymers used in this study are listed in Table 1, with melting temperature (T_m), glass transition temperature (T_g), melt flow index and flexural elastic modulus (E_f).

Blend preparation

Blends were prepared using a modular intermeshing corotating twin-screw extruder, Werner-Pfleiderer ZSK-30. The mixing conditions were set as follows: 150 rpm of screw speed, output rate of 4 kg/h, and 200°C of processing temperature along the extruder profile. After blending, strands were cooled in a water bath and subsequently pelletized. The screw configuration used a typical combination of conveying and kneading elements (see Fig. 1); the feed zone has elements with long and short screw pitches to transport and compress the granular solid material, respectively. The mixing zone has two elements of kneading KB45/5/42, followed by an element with a reverse pitch which tries to pump the material backwards and contributes to the total melting of the material due to the gradient pressure built up. Finally, in the pumping zone were placed kneading disc with short widths to promote dispersion and distribution of the second phase, followed by conveying elements with short pitches to generate enough pressure to push the material through the die. This screw arrangement was previously used to study morphological development in different kinds of blends[12,13].

Three different blending sequences were implemented to prepare all quaternary blends: (BS1) simultaneous mixing of the four components (HDPE +LDPE +PP +PS), (BS2) binary blend of (HDPE/LDPE) mixing with (PP/PS) blend, and (BS3) preparing HDPE/LDPE/PP ternary blend followed by mixing with PS pellets.

To study the influence of PS concentration, blends were prepared by adding 5 and 10% of PS to 73.40% of HDPE, 20% of LDPE, and 6.6% of PP in weight percentage. This composition was defined as the optimal point (related to mechanical properties) according to response surface in a design of experiments.

Characterization

The rheological properties of raw materials and blends were measured using a Malvern Kinexus Pro rheometer in parallel plate configuration. The viscosity (η), were performed in oscillatory mode with constant shear stress amplitude. The frequency sweep varied from 0.1 to 100 Hz at 200°C, corresponding to the extrusion temperature. All measures were within the linear viscoelastic regime and 75% of the maximal stress was taken to make the frequency sweep measurements. It was assumed the Cox–Merz rule valid.

In binary blend morphology[1,2,14,15], morphology blend can be determined by the viscosity ratio p, defined

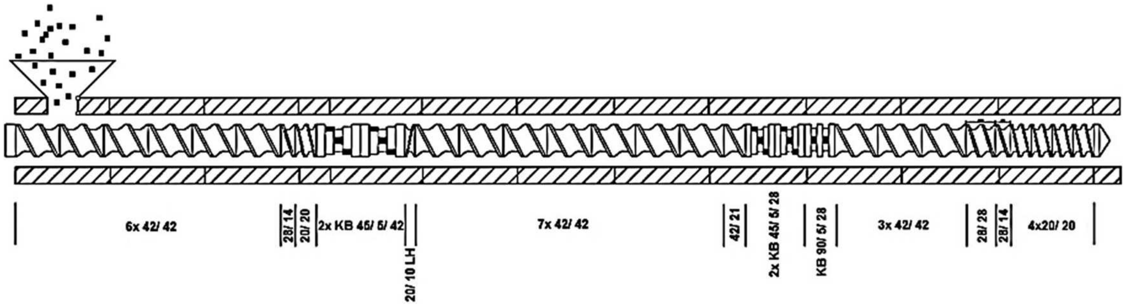


Figure 1. Blending sequence and screw configuration used for the processing of the blends.

as: $p = \frac{\eta_d}{\eta_m}$, ($\eta_d$ is the viscosity of the disperse phase and η_m is the viscosity of the matrix). When $p \ll 1$, the droplet is deformed into fibrils that finally fall apart into single droplets, between $0.1 < p < 1$ droplet dispersion by shear takes place most easily; and when $p = 0.7$ droplet is deformed into a long cylindrical fibril. Finally, when $p = 1$ droplet is broken up into two identical smaller droplets[1].

The morphology of the quaternary blends was examined by means of scanning electron microscopy (SEM, Jeol JSM-6490). All samples were immersed in liquid nitrogen and fractured in the longitudinal direction of the extrusion. PS phase was remove to create more contrast, fractured sample was immersed in chloroform at 50°C for 14 h and subsequently dried in a vacuum oven during 6 h at 60°C.

A semi-automatic image analyzer software (Image J) was used to quantify the diameter and size distribution of the dispersed PS phase. Three SEM micrographs per each blend were analyzed, about 200–400 dispersed domains were considered to calculate the result. When the shear rate is too high, the fibrils can break up into fine drops; this is why we analyzed all the spherical disperse phase into the blends. A morphological descriptor was used to determine the circular form $F = 4\pi A/P^2$; where A is the area and P the perimeter. For a completely round particle, $F = 1$. A was also used to calculate the diameters for spherical particles (d_i), according to $d_i = \sqrt{4/\pi . A}$, and these results were used to determine the average diameters in number d_n [Eq. (1)] and volume d_v [Eq. (2)].

$$d_n = \frac{\sum_i d_i}{n}, \tag{1}$$

$$d_v = \left(\frac{\sum_i d_i^3}{n}\right)^{1/3}, \tag{2}$$

with n as the number of particles.

Mechanical properties were carried out in an Instron 3366, following the ASTM D790-07 plastic flexural three point bend test. Each test corresponds to five probes with 127 × 12.7 × 3.2 mm and 1.30 mm/min was used. The test ended when the material had achieved 5% deflection or it broke.

Results

Rheological behavior

HDPE present the higher viscosity, PS and PP have the lower value in the whole range of shear rates (Fig. 2a). HDPE/LDPE blend has higher viscosity than PP/PS blend (Fig. 2b). However, the difference between HDPE/LDPE/PP and PS is lower, compared to the differences between the other systems that have been considered (Fig. 2c).

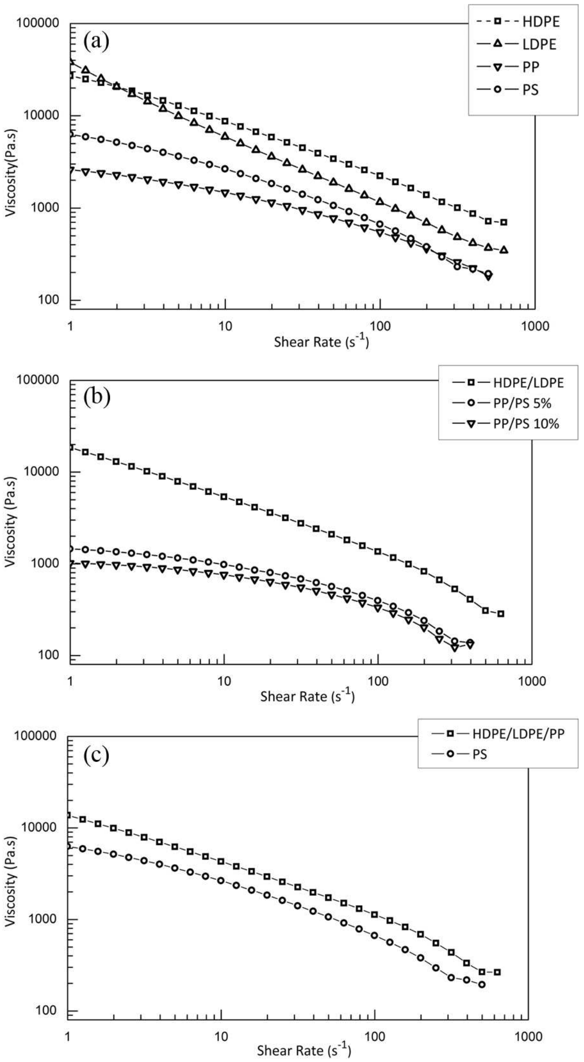


Figure 2. Viscosity as a function of shear rate measured at 200°C for (a) pure materials-BS1, (b) BS2, and (c) BS3.

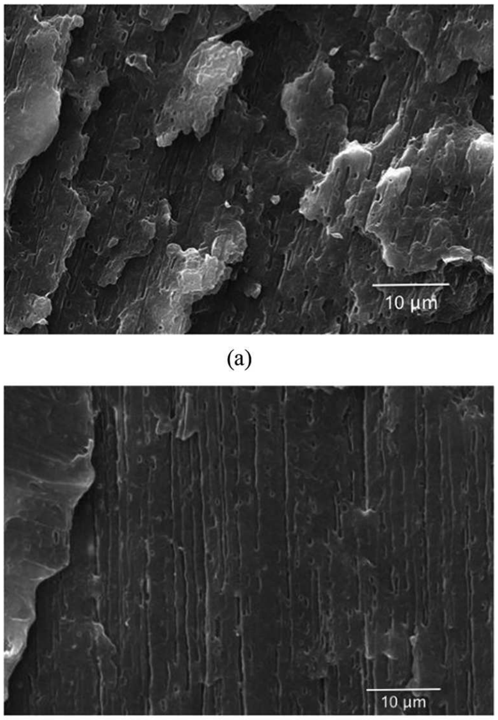
Morphology development

For all blends, viscosity ratio (p) was less than 1 (see Table 2). In this case, high viscous matrix promotes deformation process in the dispersed phase.

In BS1, PS forms elongated fibrils in the longitudinal direction of the extrusion process and also forms

Table 2. Viscosity ratio and morphology type for all blends.

Blend sequence	p (PS 5 wt%)	p (PS 10 wt%)	Morphology type
BS1 $P = \eta_{PS}/\eta_{HDPE}$	0.27	0.27	$p < 1$ Elongated fibrils
BS2 $P = \eta_{HDPE/LDPE}/\eta_{PP/PS}$	0.29	0.24	$p < 1$ Elongated fibrils
BS3 $P = \eta_{HDPE/LDPE/PP}/\eta_{PS}$	0.55	0.55	$p < 1$ Elongated fibrils

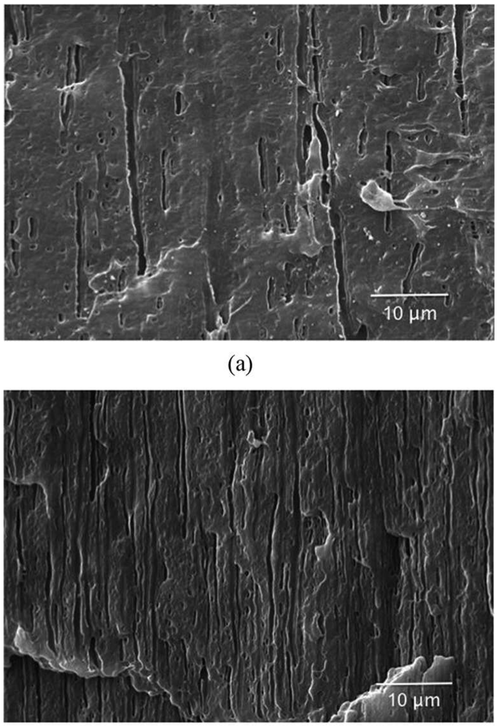


(a)

(b)

Figure 3. Morphology of quaternary blend in BS1. (a) 5 wt% PS and (b) 10 wt% PS.

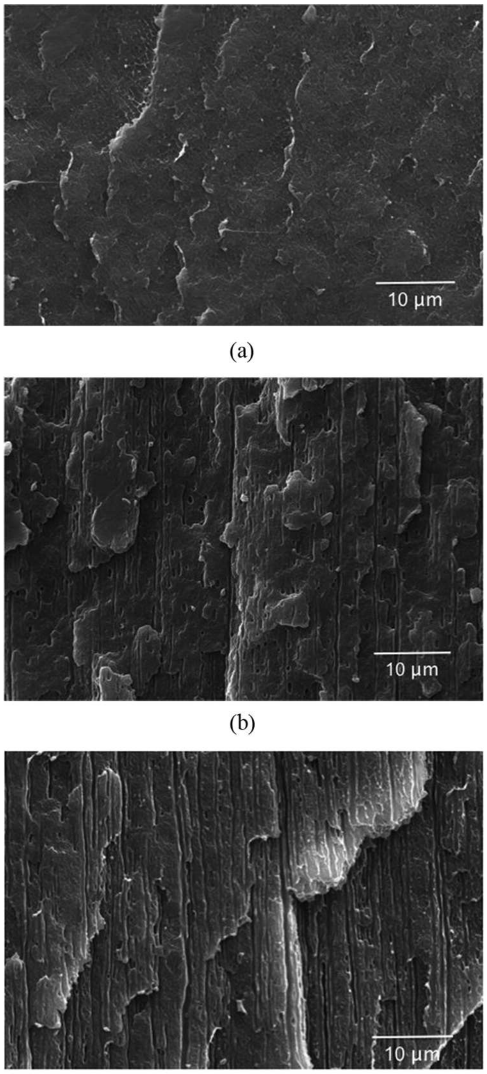
spherical particles, originated from the breaking up of fine fibrils (Fig. 3). In 10% PS (Fig. 3a), there are more and larger fibrils than in 5% PS blend (Fig. 3b).



(a)

(b)

Figure 4. Morphology of quaternary blend in BS2. (a) 5 wt% PS and (b) 10 wt% PS.



(a)

(b)

(c)

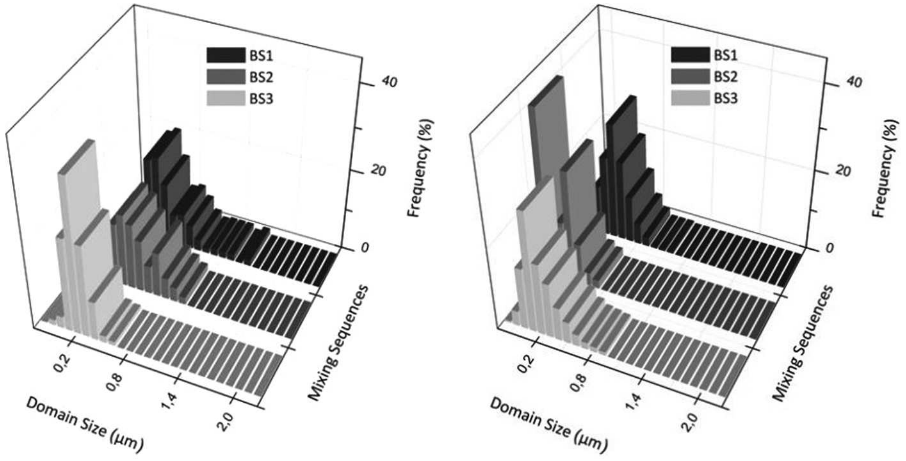
Figure 5. Morphology of quaternary blend in BS3. (a) HDPE/LDPE/PP blend, (b) 5 wt% PS, and (c) 10 wt% PS.

In this sequence (BS2), the images present more fibrillar morphology than in BS1 (Fig. 4) and 10% PS has larger and packaged fibrils.

For BS3, in Fig. 5. We present the image of the ternary blend (HDPE/LDPE/PP) with no clear morphology but with a rough surface (Fig. 5a). When PS is added, the fibrils appear again in a rough matrix (Fig. 5b and 5c.)

Because in all the SEM images, we can see drops, and we counted the quantity and the size of the drop generated in each blend sequences. All blends present a narrow size distribution (Fig. 6). BS3 with 5% PS and BS2 with 10% PS have the higher quantity of drops. Besides, BS2 with 10% presents a bimodal distribution.

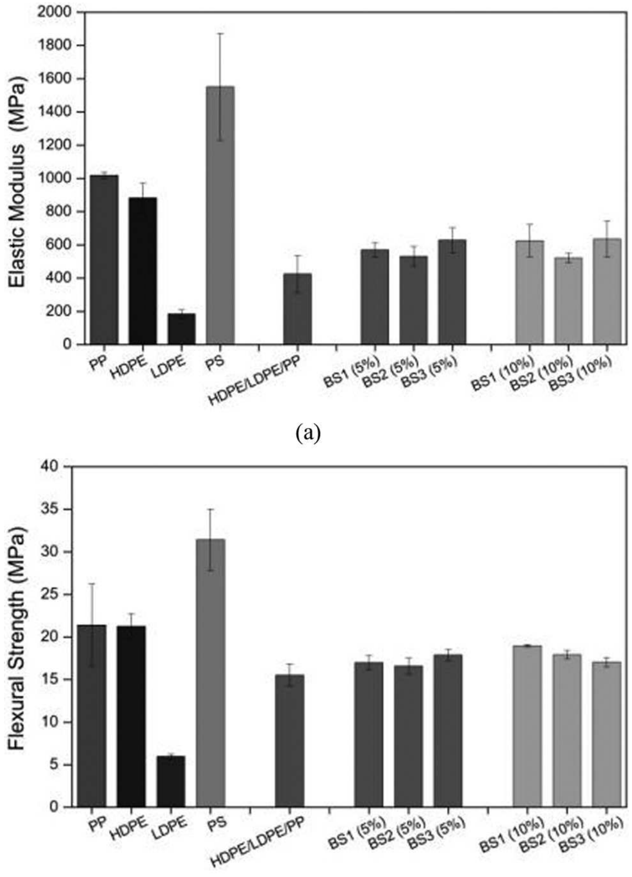
Fibrillar morphology affects the mechanical properties; in Figure 7, we present the modulus and flexural strength of the materials. Elastic modulus increase



(a) (b)

Figure 6. Particle size distribution of PS dispersed phase: (a) 5 wt% PS and (b) 10 wt% of PS.

37% with 5% PS and 40% with 10% PS with respect to ternary blend. In relation to flexural strength, quaternary blends increase 10 and 17%. However, we believe that this number could be higher, because the probe test manufacturing changes the morphology and the fibrillar morphology disappears, so these values are due to droplet morphology.



(a)

(b)

Figure 7. a) All materials and blends elastic modulus and b) all materials and blends flexural strength.

Discussion

We found that the order of mixing affects the size of the dispersed PS phase. BS1 morphology, with all polymers added at the same time, has a higher quantity of fibrillar structures and they are thicker and longer. For BS2, viscous (HDPE/LDPE) and lubricant polymers (PP/PS), the lubricant effect of the lower viscosity blend could be greater, but the viscosity ratios are not very different from BS1. In BS3, polyolefins and PS, viscosity ratio was near to 0.7, in contrast to BS1 and BS2. This is why micrographs show a well-defined fibrillar morphologies. Adding 10 wt% of PS shows an increase in the number of fibrils, which makes a greater packing of them.

Image analysis confirmed that the number of fibrils in BS3 was higher (on average 160 fibrils), and also longer, than those obtained in BS1 and BS2. Although the dispersed phase preferentially forms elongated structures, a big number of spherical particles or droplets of PS also coexist in all quaternary blend morphologies, due to the breaking up process. Particularly, a smaller number and a lower size of particles are given in BS3 with 5 wt% of PS and BS2 with 10 wt% of PS. The mixing order affects the size of the dispersed PS phase. Furthermore, these histograms give an approximately normal distribution of PS particles, and the particle size distributions are narrow in all cases and size distribution is nearby to 1 (see Table 3).

Dealing with flexural behavior, all blend results are among the value of the originals polymers. However, it seems that fibrillar morphology does not improve

Table 3. Size of the dispersed PS phase in terms of d_n and d_v as a function of blending sequences and PS concentration.

Blending sequence (%)	d_n (μm)	d_v (μm)	Size distribution
BS1 (5)	0.63	0.68	1.08
BS2 (5)	0.57	0.64	1.12
BS3 (5)	0.47	0.49	1.04
BS1 (10)	0.42	0.47	1.12
BS2 (10)	0.24	0.26	1.08
BS3 (10)	0.45	0.49	1.08

the mechanical data, and quaternary blend values are similar to the ternary blends (the increasing is due to the quantity of PS added). In this case, we took SEM images of the probe after the test, and we saw that the fibrillar morphology disappeared, as a consequence of the thermal process used to manufacture the standard probe test (compression molding). This also could explain why the blending sequences did not present any mechanical difference among all the blends.

Blending sequences affect morphology, which has to be kept in the final product, if we want to see changes in the mechanical properties.

Conclusion

This study evaluates the influence of different blending sequences in the morphology of quaternary blends of polyolefins with PS. High viscous matrices ($p < 1$) enhance deformation and break up processes, displaying PS fibrils and finer dispersions.

Blending sequences of ternary blend create a viscosity ratio (0.55) capable to promote well-defined fibrillar morphology. According to these experimental observations, we can conclude that Taylor's theoretical prediction can be applied to these multicomponent polymer blends system.

Our results suggest, to blend first a similar polymer family and after that, to add the different polymer. Also, it is necessary to have in mind that blend morphology created in an extrusion process is very sensitive to further thermal treatments.

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