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Lama Elias, Philippe Cassagnau, Françoise Fenouillot, Jean-Charles Majeste. Morphology and rheology of immiscible polymer blends Filled with silica nanoparticles. CFM 2009 - 19ème Congrès Français de Mécanique, Aug 2009, Marseille, France. hal-03391498

**HAL Id: hal-03391498**

**<https://hal.science/hal-03391498v1>**

Submitted on 21 Oct 2021

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# Morphology and rheology of immiscible polymer blends Filled with silica nanoparticles

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## Abstract :

Two types of pyrogenic silicas (hydrophilic and hydrophobic) were added to polypropylene / polystyrene (PP/PS) and polypropylene / poly(ethylene-co-vinyl acetate) (PP/EVA) blends. The mixing procedure was varied, then the morphology were observed and rheological data collected. First of all, a significant reduction of the dispersed phase droplets size was observed in the presence of only 3wt% of both type of silica. Microscopy proved that the hydrophilic silica tends to confine in the more polar PS or EVA phase whereas hydrophobic one was located at the PP/PS interface and in the PP phase. The interface between PP and PS has been changed by an interphase PP/Silica/PS of a hundred of nanometers thick. With the blending procedure consisting in pre-blending silica particles in PP matrix, a migration of hydrophilic silica from PP phase toward PS or EVA domains was observed. The quantitative analysis of the rheological experimental data was based on the framework of the Palierne model, extended to filled immiscible blends. Due to the partition of silica particles in the two phases and its influence on viscosity ratio, limit cases have been investigated. Assuming that the hydrophilic silica particles are totally located in the PS phase, the interfacial tension was calculated to be reduced from 2.15 to 0.085 mN/m. The case of hydrophobic silica was more difficult to model since the existence of a thick interface cannot be taken into account by the model. The hypothesis that silica is homogeneously dispersed in PP matrix is much closer to the actual situation and the model shows that the interfacial tension is not reduced in this case. We concluded that stabilization mechanism of PP/PS blend by hydrophilic silica is the reduction of the interfacial tension whereas hydrophobic silica acts as a rigid layer preventing the coalescence of dispersed droplets.

## Mots clefs : Silica nanoparticles, blends, lineair viscoelasticity

## 1 Introduction

Generally, most of polymer blends are incompatible, resulting in materials with weak interfacial adhesion and thus poor mechanical performances, therefore, the greatest challenge in the field of the multiphase polymer blend research is the manipulation of the phase structure via a judicious control of the interfacial interactions between the components. One of the classical methods to ensure adhesion between the phases (reduction the interfacial tension) is the use of third component, a compatibilizer, which results in a finer and more stable morphology, better adhesion between the phases and consequently better mechanical properties of the final product. Recently, an original concept of compatibilization by using rigid nano-particles like silica nano-particles has been proposed. Nano-SiO<sub>2</sub> particles in a wide range of size and with a variety of surface treatments. The considerable specific surface area of these nano-particles (50-400 m<sup>2</sup>/g), the type of silica nano-particles the presence of functional groups silanol, siloxane, and the concentration of silica in the blend, play a major role in their rheological behaviour and their dispersions in the blend. The main objective of our current works is to investigate the effect of silica nano-particles on the morphology and the rheological properties of immiscible polypropylene / polystyrene (PP/PS) and polypropylenes / poly(ethylene-co-vinyl acetate) (PP/EVA) polymer blends and more specifically to understand the influence of the nature of the filler on the interfacial stress ( $\alpha/R$ ), with the help of the Palierne model [1] as the general framework of this quantitative study.

## 2 Experimental

### 2.1 Materials

PP was supplied by Atofina (PPH 7060) with a melt flow index MFI=12 g/10 min. The molecular weights are:  $M_n= 67,300\text{g}\cdot\text{mol}^{-1}$  and  $M_w= 273,000\text{ g}\cdot\text{mol}^{-1}$ . The PS (LACQRENE Cristal PS 1960N) with  $M_n= 49300\text{ g}\cdot\text{mol}^{-1}$  and  $M_w= 93500\text{ g}\cdot\text{mol}^{-1}$ , and Two poly(ethylene-co-vinyl acetate) (EVA), of different molar masses have been used (table1) are supplied by Arkema. The amount of acetate groups contained in these copolymers is 28% by weight. The zero shear viscosities of these EVA are reported in table 1 at  $T=200^\circ\text{C}$ . Figure 1, 2 shows respectively the variations of the complex shear modulus ( $G^*(\omega)=G'(\omega)+jG''(\omega)$ ) of PP, PS at the temperature  $T=200^\circ\text{C}$ , and the variations of the absolute complex viscosity of EVA03, and EVA420 at the temperature  $T=200^\circ\text{C}$ . The silica content was 3 wt% of the total material. Two types of nanosilica ( $\text{SiO}_2$ ) were used. A hydrophilic pyrogenic silica, HDK<sup>®</sup> N20, with a specific surface area of 170 - 230  $\text{m}^2/\text{g}$  and a hydrophobic nanosilica, HDK<sup>®</sup> H20 RC, having the same specific surface area treated with trimethoxyoctylsilane. The two types of silica are aggregates of primary spherical particles having an average diameter of 12 nm. Both of them were kindly supplied by Wacker Corp.

Polymer	Melt flow index	$M_w$ ( $\text{g mol}^{-1}$ )	Zero shear viscosity $\eta^0$ (Pa.s)
PP	12	273 000	2500
PS	12	93500	1000
EVA 2803	3	53500	3100
EVA 28420	420	12000	100

Table 1: Molecular weight and zero shear viscosity of PP and EVA samples at  $T = 200^\circ\text{C}$

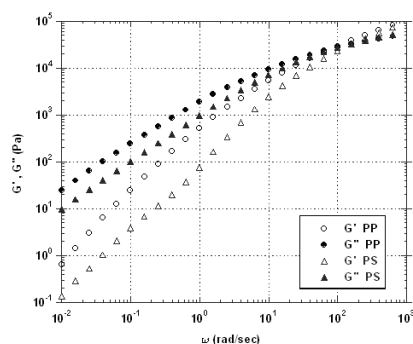


Fig.1- Viscoelastic behaviour of PP and PS at  $T=200^\circ\text{C}$

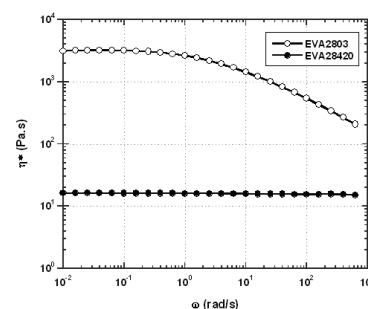


Fig. 2 - Variation of the complex shear viscosity of poly(ethylene-vinyl acetate)

### 2.2 Compounding procedure

All blends and composites were prepared by using DSM twin-screw mini-extruder. The extruder was filled with 13g of material. The screw speed was 120 rpm. All the experiments were performed under nitrogen atmosphere in order to prevent oxidative degradation. We used two blending procedures.

1) The three components (PP, PS, silica particles) and (PP, EVA, silica particles) were loaded to the mixing chamber simultaneously and compounded at 200°C for 5 min.

2) The silica was pre-compounded with PP at 200°C for 5 min. Then the obtained material (PP/silica) was blended with the second polymer during a second extrusion step.

The blends were then compression moulded using a laboratory press at 200°C for 3 min into 1 mm thick sheets and then cooled to room temperature.

These samples were analysed in dynamic mode of shearing on a rheometer AR2000 (TA Instrument) using a parallel plate geometry with 25 mm diameter. All experiments were carried out at the temperature of 200°C in the frequency range  $0,01 < \omega \text{ (rad.s}^{-1}\text{)} < 628$ . All experiments were performed in the domain of the linear viscoelasticity and under nitrogen atmosphere in order to prevent thermo-oxidative degradation.

## 2.3 Morphology characterization

The morphology of the virgin blends and filled blends, was investigated by Scanning Electron Microscopy (SEM) using a Hitachi S800 model. The samples were fractured in liquid nitrogen. The PS and EVA phases was selectively extracted by tetrahydrofurane (THF) solvent at room temperature to enhance the contrast. The fractured surfaces were sputter-coated with gold/palladium (50/50). Furthermore, to observe the location of silica nano particles in more detail, Transmission Electron Microscopy (TEM) was also carried out on blend samples. Cross sections of the moulded blend were obtained by slicing the sample into thin films of about 50nm thickness. Morphology of these samples were then examined using a Philips CM120 transmission electron microscopy.

The droplet size was determined by using image analysis . The diameter of each droplet ( $R_i$ ) was calculated from the corresponding area ( $A_i$ ). Typically, 300 particles were analyzed per sample. Corrections to the particles size were performed using Schawartz-Saltykov [2].

## 3 Results and discussion

### 3.1 Morphology of PP/PS blends

First of all we report some preliminary results on PP/PS blend. From an experimental point of view, polypropylene (PP) and polystyrene (PS) were used with two types of silica, hydrophilic (fumed silica) and hydrophobic silica, treated with trimethoxyoctysilane. The typical phase morphologies of a virgin and silica nano-particles PP/PS (70/30) blends are shown in Fig.3. The results show that the morphology of the virgin blend was significantly changed and particles size was dramatically reduced upon the addition of silica nanoparticles. The particle average diameter size of PS phase decreased from 3,70  $\mu\text{m}$  (Fig. 3-a) to 0.85  $\mu\text{m}$  upon the addition of 3 wt% of hydrophilic silica nano-particles(Fig.3-b), The addition of 3 wt% of hydrophobic silica leads also a remarkable decrease of PS particles size to 1.25  $\mu\text{m}$ .

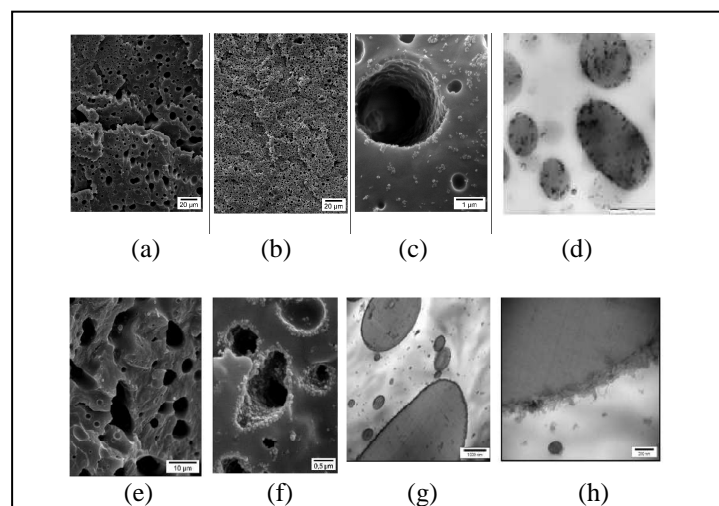


Fig 3 - Morphology of PP/PS [70/30] blend. a) Virgin blend, b) 3% hydrophilic silica, c) Zoom of image b), d) TEM image showing the confinement of the hydrophilic silica in the PS droplets, e) Virgin Blend, f) SEM image showing the silica at the PP/PS interface, g) TEM image showing the confinement of the hydrophobic silica at the PP/PS interface, h) zoom of image g).

### 3.2 Morphology PP/EVA blends

The effect of silica nano-particles on the morphology of PP/EVA03 blend is shown in Figure 4. The presence of silica particles reduces significantly the coalescence phenomena and the EVA domain size is decreased by a factor two approximately as observed by comparing the micrographs a) and b), e) and f) in figures 4 and figure 5. Clearly, silica particles are efficient at producing a relatively uniform distribution of drop sizes and the distribution shifts to smaller diameter. These results confirm that the incorporation of silica nano articles decrease the EVA droplets and results in finer dispersion of EVA in PP matrix wherever the kind of EVA and the type of silica nano particles (hydrophilic or hydrophobic).

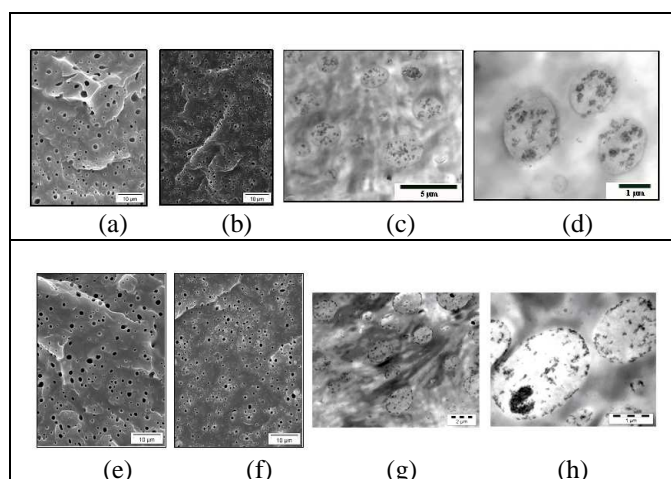


Fig. 4 - Morphology of PP/EVA03 [80/20] blend. a) Virgin blend, b) 3% hydrophilic silica, c), d) TEM image showing the confinement of the hydrophilic silica in the EVA03 droplets, e) Virgin Blend, f) SEM image showing the silica at the PP/EVA03 interface, g) TEM image showing the confinement of the hydrophobic silica at the PP/EVA03 interface, h) zoom of image g).

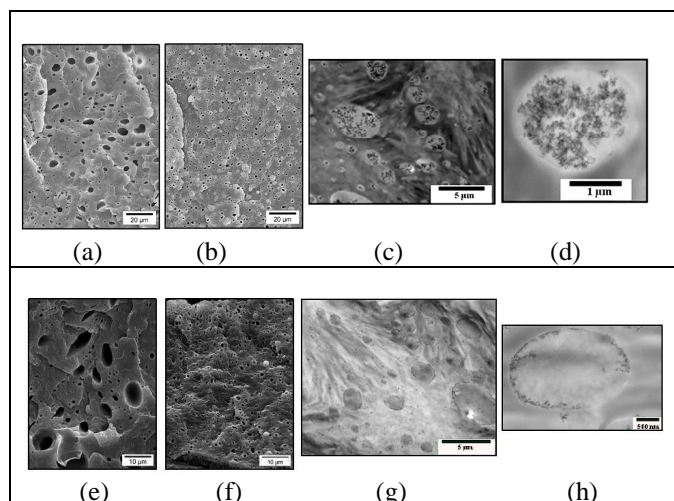


Fig. 5 - Morphology of PP/EVA420 [80/20] blend. a) Virgin blend, b) 3% hydrophilic silica, c), d) TEM image showing the confinement of the hydrophilic silica in the EVA420 droplets, e) Virgin Blend, f) SEM image showing the silica at the PP/EVA03 interface, g) TEM image showing the confinement of the hydrophobic silica at the PP/EVA420 interface, h) zoom of image g).

Table 2, shows the effect of silica nano particles on the average radius ( $R_v$ ) of RVA03 and EVA420 droplets.

blends	$\alpha/R_v$	$R_v$	$\alpha$
	mN/m <sup>2</sup>	$\mu\text{m}$	(mN/m)
PP/EV03 Virgin blend	920	0.81	$0.75 \pm 0.15$
PP/EVA03 +3% SiN20	550	0.46	$0.25 \pm 0.05$
PP/EVA03 +3% SiH20	525	0.57	$0.30 \pm 0.01$
PP/EVA420Virgin blend	425	2.2	$0.94 \pm 0.17$
PP/EVA420+ 3% Si N20	600	0.56	$0.34 \pm 0.08$
PP/EVA420 +3% Si H20	375	0.48	$0.81 \pm 0.17$

Table 2 - Average radius ( $R_v$ ) of EVA03 and EVA420 droplets in PP matrix. Composite blends have been filled with 3% wt hydrophilic silica (SiN20) and SiH20 (hydrophobic). The ratio  $\alpha/R_v$  was calculated from the Palierne model.  $\square$  is the interfacial tension calculated from  $\alpha/R_v$  values.

### 3.3 Rheological behaviour and modelling of PP/PS/silica nanocomposites

The viscoelastic behaviour of immiscible polymer blends is studied for years now. The present blend has been chosen so that the secondary plateau is well visible on the moduli (figure 6-a). This shoulder is attributed to the shape relaxation of the dispersed PS droplets. The corresponding relaxation time is generally determined by calculating the continuous relaxation spectrum based on the dynamic moduli [3,4]. In a straightforward and simplest manner, the variation of  $h''(\omega)$  describes qualitatively the relaxation spectra of the blend. As shown in Fig. 2-b, a pronounced relaxation peak, reflecting the shape relaxation of the droplets, is clearly seen in the domain of low frequencies.

Furthermore, since the emulsion model of Palierne [1] has been successfully applied in the past to obtain morphological and interfacial information on immiscible blends, we have used it to calculate the ratio  $a/R_v$  (interfacial tension over the volume average droplet radius) from the best fit of the experimental and calculated dynamic moduli (see Fig.6). Following this, the interfacial tension of PP/PS blend can be derived as  $R_v$  has been measured with the help of the morphology pictures (Fig. 1). We finally found a  $\approx 2.15$  mN/m. In order to confirm this result, the interfacial tension was also optically measured from a deformed drop retraction experiment [5]. This method yields to a  $\approx 2.50$  mN/m. Actually, this value is approximately twice lower than the value generally reported in the literature. Depending on polymer mass molar and temperature, the reported values for interfacial tension between PP and PS range from 4 to 7 mN/m [4, 6, 7]. This difference between our result and those from the literature may be attributed to commercial nature of the polymers used in the present study. Actually, PP and PS are containing additives for processing operations and for stabilization. Consequently, as suggested by Huo et al [4], the values of  $a/R$  are generally used in order to avoid any ambiguity with the interfacial tension. In the present study, we find  $a/R_v \approx 660$  mN/m for neat PP/PS.

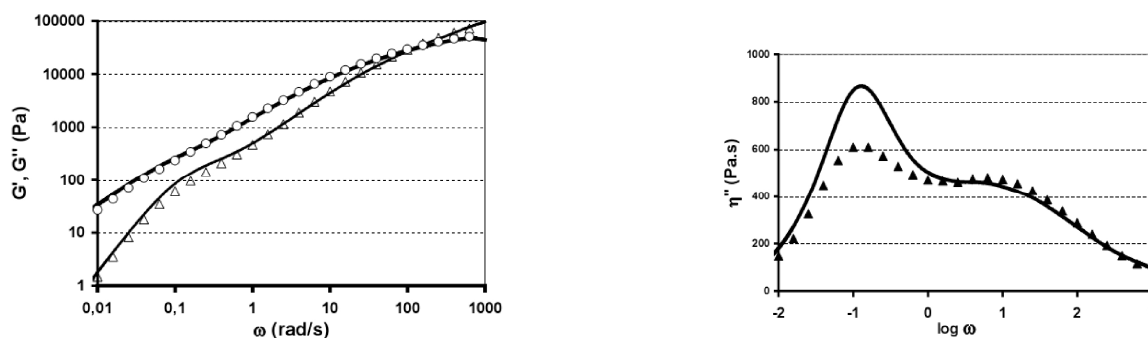


Fig. 6 - Viscoelastic behaviour of PP/PS 70/30 blend, at  $T=200^\circ\text{C}$ : a) Frequency dependence of  $G'(w)$  b) Frequency

dependence of  $\eta''(\omega)$  Solid line represents the Palierne's model.

The presence of silica nanoparticles in the blend will obviously alter the viscoelastic properties. They should be influenced not only by the percentage of silica but also by the way they are distributed in the two-phase system. However, changing the blending procedure (mixing PP, PS and silica simultaneously or silica pre-mixed in PP Phase) does not affect significantly experimental rheological behaviours for blends filled with hydrophilic silica. This experimental result confirms our finding from TEM pictures, the final dispersion state of silica and morphology of the blend does not depend on the preparation procedure. Vermant et al [8] came to the same conclusion for PIB/PDMS blend. Nevertheless, when 3 wt% of silica (hydrophilic or hydrophobic) are added in the blend, the relaxation of the PS droplets is shifted to lower relaxation times compared with the neat PP/PS blend. In other words, the faster drop relaxation qualitatively means [1] that the interfacial forces increase when silica fillers have been added in the blend.

From the modelling point of view, further quantitative explanations on the role of inorganic fillers in immiscible blends can be then expected from the Palierne model. The model was successfully adapted [9,10] to take into account the three phases: molten phase dispersed in a molten matrix filled with a third solid phase. Actually, this model assumed that the contribution of a solid phase dispersed in viscoelastic matrix constituted itself by two molten phases, could be expressed from the Einstein's law in the same way as the expression of the complex shear moduli of filled system. Depending on silica nature and according to SEM and TEM observations, the following particular rheological cases have been investigated assuming the partition of the silica between PP and PS phases: Hydrophilic silica: 1) The silica is homogeneously dispersed in the blend so that its concentration in PP and PS phases is rigorously 3 wt% corresponding to the macroscopic silica concentration, 2) the silica is partitioned in the blend, mainly in the PS phase so that the concentration of silica in PP and PS phases is 0 wt% and 10 wt% respectively. Hydrophobic silica: Compared with hydrophilic silica, a third assumption was made, 3) The silica is partitioned in the blend, mainly in the PP phase so that the concentration of silica in PP and PS phase is 4.2wt% and 0wt% respectively. A very important point is that the silica play a role not only on the interfacial properties but also on the viscosity ratio of the blend. Which of those parameters is determinant here? This is quite different from the compatibilization obtained with block copolymers where the viscosity of the phases is not modified. Thus, it is attractive to express from Palierne model the  $\alpha/R_v$  ratio and subsequently the interfacial tension of filled PP/PS blends. However, this interfacial tension must be actually viewed as an apparent interfacial tension since it is calculated from the relaxation of PS droplet more or less covered by silica particles. With hydrophilic silica the interface is only partially occupied by the inorganic particles while hydrophobic silica almost totally covers the interface and forms a 100 nm thick interphase. Since the Palierne model does not permit to take into account a "solid" layer around the dispersed PS domains we suspect that it will be difficult to apply it to the blend filled with hydrophobic silica.

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