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Immiscible polymer blends stabilized with nano-silica particles: Rheology and effective interfacial tension

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ABSTRACT

The effect of inorganic silica nanoparticles on the morphology and viscoelastic properties of polypropylene/poly(ethylene-*co*-vinyl acetate) (PP/EVA) immiscible blends has been investigated. Different EVA with different molar masses were used in this study. Virgin and filled blends were prepared by using a twin-screw mini-extruder. Microscopy studies revealed a significant change in morphology of PP/EVA blend in the presence of silica nanoparticles. Also, the images proved the migration of silica nanoparticles toward EVA phase, and to the interface.

The quantitative analysis of the rheological experimental data was based on the framework of the Palierne model, extended to filled immiscible blends. Based on this model, a method of determination of the interfacial tension from rheological measurement has been addressed with an improved accuracy. Even if silica mainly plays a thermodynamic role in the stabilization mechanism by decreasing the effective interfacial tension, the influence of particular rheological conditions and the structure of the phases must be taken into account for a complete understanding of the final morphology of such systems.

1. Introduction

The stabilization of emulsions by incorporating colloidal particles is known since one century with the pioneer works of Ramsden [1] and Pickering [2]. Few years ago, the research group of Binks has intensively studied the stabilization and phase inversion in emulsion by nano-silica particles. For instance, their researches have been focused on the use of colloid silica particles to stabilize different oil–water emulsions [3,4,5]. As discussed by Vignati and Piazza [6] the most probable mechanism of morphology stabilization is a steric hindrance or surface rheology effects due to the particle adsorption at the interface rather than a decrease of the interfacial tension between the two liquids. Regarding high viscous emulsions such as immiscible polymer blends, the effect of colloidal particles on the morphology development has only been recently investigated but is currently the topic of intense investigations. Several researchers have reported both experimental results and theoretical predictions that the addition of nanoscale fillers affects the dynamic phase behavior and morphology of blends. From experimental observations, the incorporation of a few percent of nano-filler during melt processing of the components causes a substantial reduction of the size of the dispersed phase. Carbon black [7–11], organoclay [12–19] and silica [20–24] particles have been used in these studies. However, the mechanisms by which particles stabilize against coalescence are not completely understood yet. Most of the authors concluded that the fillers act as physical barrier due to their accumulation at the interface, which prevent the coalescence of the dispersed phase. More specifically, Thareja and Velankar [22] proposed a “particle bridging” mechanism based on the observation of a gel behavior in the rheology at low frequencies. This gel-like behavior was attributed to the formation of a particle network that bridges the droplets. Such mechanism is well known in conductive composite polymers [8] and is generally called double percolation. Consequently, this mechanism depends on filler concentration and on volume fraction of the dispersed phase. Actually, although this mechanism cannot be totally excluded, its influence on droplet stabilization is not generally the dominant mechanism. For instance, Elias et al. [23] and Vermant et al. [21] observed no upturn in the absolute complex viscosity in the domain of the accessible frequency range.

More theoretically, Nesterov and Lipatov [25] and Lipatov et al. [26] studied the influence of fumed silica particles on the phase

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diagram behavior of polymer blends with lower critical solution temperature (LCST). They came to the conclusion that the total free energy of a blend system should also include the interaction parameters between the polymers and the inorganic filler surface. In other words, addition of a filler S to A–B blend stabilizes the morphology. Actually, the solid particles act as a compatibilizer by adsorbing A and/or B polymers on their surface. To play this role the inorganic phase should have the largest possible surface area and should be able to disperse very well in the two phases. From this statement, Si et al. [16] proposed to use organoclay rather silica particles to study this effect in more detail. Indeed, in contrast to fumed silica, exfoliated clays are composed of nanoscale tactoids of great surface available for interaction with polymers. Finally they demonstrated that blend compatibility can be improved with dispersion of organoclays by melt mixing. Furthermore, they attributed this compatibility mechanism to the formation of in situ grafts during mixing processing. Even chain grafting is questionable in their work, some authors argued that the key factor for compatibilization efficiency of the organoclay is the initial interlayer spacing and its ability to reduce the interfacial tension and average particle size by chain adsorption. Hong et al. [17,18] showed that the effect of the organoclay on the reduction in the droplet size is governed by the location of the organoclay which is determined by the difference in affinity of component/clays system. More precisely Ray et al. [12] showed that the compatibilization process was really more efficient when PP is grafted with maleic anhydride that ensures interaction with clay side OH groups.

However, the use of nano-silica particles can be motivated as they exist in a wide range of size (specific area: 50–400 m^2/g) and with a variety of surface treatments from hydrophilic to hydrophobic. Furthermore, nano-silica particles are used as filler in various industrial applications to control rheological properties. In our previous papers [23], we investigated the role of silica nanoparticles on the morphology of immiscible PP/PS blend (non-polar polymers). The main objective of this work was to address a quantitative analysis of the rheological experiment based on the framework of the Palierne model. As a result, we concluded that the mechanism of morphology stabilization of PP/PS blend by hydrophilic silica was the reduction in the effective interfacial tension whereas hydrophobic silica particles act as a rigid layer preventing the coalescence of PS droplets. However, the development of Palierne model to filled immiscible blends is not straightforward and requires some strong assumptions on the viscoelastic properties of polymer phases filled with the silica particles. The objective of the present work is to revisit the development of the Palierne model to filled polymeric emulsions. On the other hand, our work is focused on immiscible blend composed of polypropylene (PP) and a copolymer of ethylene and vinyl acetate (EVA) as we look to investigate the effect of the dispersed phase polarity and viscosity.

2. Experimental part

2.1. Materials

PP was supplied by Arkema (PPH 7060) with a melt flow index MFI = 12 g/10 min. The molecular weights are: $\overline{M}_n = 67,300\ g\ mol^{-1}$ and $\overline{M}_w = 273,000\ g\ mol^{-1}$. The zero shear viscosity at $T = 200\ ^\circ C$ is $\eta_0 = 2500$ Pa s. Two poly(ethylene-*co*-vinyl acetate) (EVA), kindly supplied by Arkema, of different molar masses have been used (Table 1). 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 $T = 200\ ^\circ C$. Fig. 1 shows the variations of the absolute complex viscosity of these polymers at the temperature $T = 200\ ^\circ C$. The silica content was 3 wt% of the total material and the proportion of EVA in PP was always 20 wt%.

Table 1

Mass average molecular weight and zero shear viscosity of PP and EVA samples at $T = 200\ ^\circ C$

Polymer	Melt flow index (g/10 min)	M_w (g mol^{-1})	Zero shear viscosity η_0 (Pa s)
PP	12	273,000	2500
EVA03	3	53,500	3100
EVA420	40	12,000	14

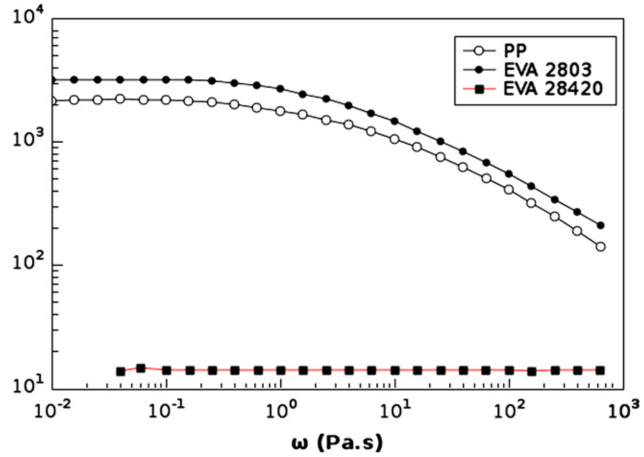


Fig. 1. Variation of the complex shear viscosity of different poly(ethylene–vinyl acetate) EVA.

Two types of nano-silica (SiO_2) were used. A hydrophilic pyrogenic silica, HDK® N20, with a specific surface area of 170–230 m^2/g and a hydrophobic nano-silica, HDK® 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.

2.2. Compounding procedure

All blends and composites were prepared by using DSM twin-screw mini-extruder. The extruder was filled with 13 g 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, 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 analyzed 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 $0.01 < \omega$ (rad s^{-1}) < 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 Hitashi S800 model. The samples were fractured in liquid nitrogen. The EVA phase was selectively extracted by tertrahydrofurane (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 nanoparticles 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 50 nm thickness. Morphology of these samples was 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 Schwartz–Saltykov method [27].

3. Results and discussion

3.1. Blends morphology of PP/EVA/silica nanocomposites

Regarding the effect of silica nanoparticles on the global morphology of PP/EVA blend, it can be observed for all systems (Table 2 and one example in Fig. 2) that the presence of silica particles reduces significantly the coalescence phenomena. More precisely, EVA domain size is decreased by a factor two or four approximately (Table 2). Therefore, 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 nanoparticles decreases the EVA droplets diameter and results in finer dispersion of EVA in PP matrix whatever the EVA viscosity and the type of silica nanoparticles (hydrophilic or hydrophobic). These results are quite similar with those obtained in the case of PP/PS blends but nevertheless, there is some difference in the case of the present system PP/EVA. First, the stable morphology is reached rapidly within 5 min mixing. On the other hand, the mixing time needed to reach the equilibrium morphology does not depend on the viscosity ratio of the two phases and the size of this final morphology is quite the same. This is really intriguing since the viscosity ratio should influence drastically the size of the dispersed phase as predicted by the dispersion mechanisms or theories [28,29].

Table 2

Average radius (R_v) of EVA03 and EVA420 droplets in PP matrix. Composite blends have been filled with 3 wt% hydrophilic silica Si N20 (hydrophilic) and Si H20 (hydrophobic). The ratio γ_{12}/R_v was calculated from the Palierne model. γ_{12} is the effective interfacial tension calculated from γ_{12}/R_v values. Silica is simultaneously added

Blends	γ_{12}/R_v (mN/m^2)	R_v (μm)	γ_{12} (mN/m)
PP/EVA03 without silica	920	0.81	0.75 ± 0.15
PP/EVA03 + 3% Si N20	550	0.46	0.25 ± 0.05
PP/EVA03 + 3% Si H20	525	0.57	0.30 ± 0.01
PP/EVA420 without silica	425	2.2	0.94 ± 0.17
PP/EVA420 + 3% Si N20	600	0.56	0.34 ± 0.08
PP/EVA420 + 3% Si H20	450	0.4	0.18 ± 0.06

Consequently, the objective here is to investigate how the presence of the silica and its localization in the biphasic blend influences the morphology. In a previous study [23], we have shown that the localization of the silica particles in PP/PS blends is governed by thermodynamics at the equilibrium. As a result, silica can be distributed non-homogeneously in the blend. Depending on their wetting ability, the silica particles are confined in one of the two phases or can be confined at the interface between the two polymers. The mode of addition of the silica seems to have weak effect on its localization.

In the present case, we found again some difference in the localization of the silica in the PP/EVA blend. Different situations are encountered. When the three components are added at the same time in the extruder (blending procedure 1), the hydrophilic

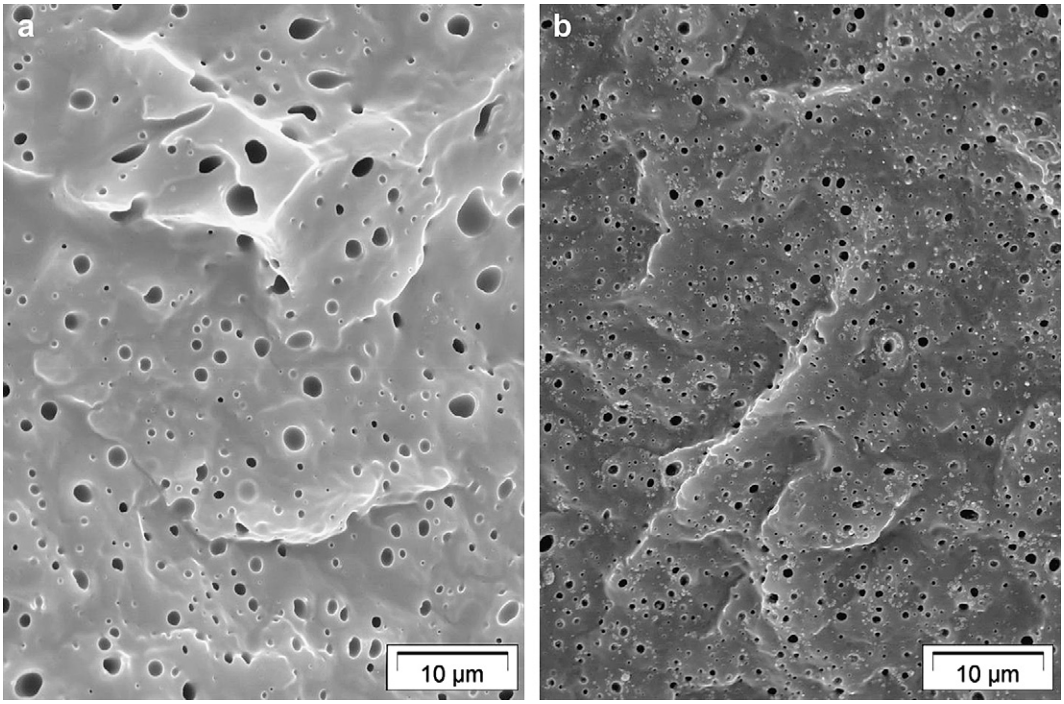
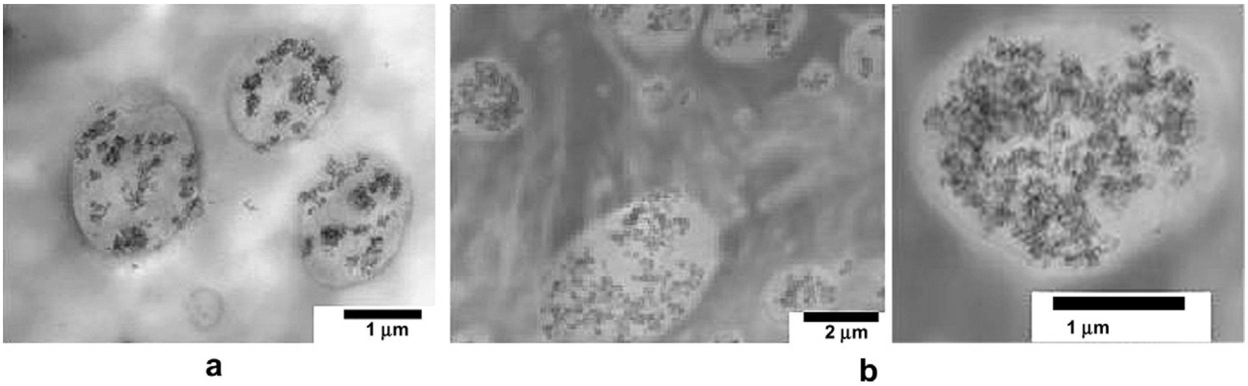


Fig. 2. Morphology of PP/EVA03 80/20 blend prepared with blending procedure 1 (the three components added simultaneously in the extruder). (a) PP/EVA blend without silica. (b) Blend filled with 3 wt% Si N20 hydrophilic silica.

N20 silica is found essentially in the EVA droplets. (Figs. 2 and 3a). On the other hand, the hydrophobic H20 silica is localized at the interface. However, we cannot observed really a layer of particles at the interface contrary to what we obtained in the previous study on PS/PP/Silica blends [23]. More precisely, TEM images (Figs. 3 and 4) show that silica particles remain close to the interface but inside the EVA side. In the case of hydrophilic N20 or hydrophobic H20 silica, pre-mixed with PP first and subsequently mixed with EVA (blending procedure 2), the silica particles initially dispersed in PP appear to be located in the EVA phase close to the interphase (Fig. 4). As previously explained, the question of thermodynamic equilibrium is central. Actually, "final localization" of the silica is what we observe after the blending procedure. However, this equilibrium may never be reached after reasonable mixing time because of the very low diffusion coefficient of the silica in viscous media. We are then obliged to conclude that the localization of the silica at the interface may only be an intermediate state. In other words, precise evaluation of the wetting parameter and all thermodynamics conditions can only predict the equilibrium localization. From an experimental point of view and the case of our processing conditions silica particles are not visible in the PP phase. Thereby, the silica particles have migrated from the PP phase toward the EVA phase in which the interactions are more favorable according to the wetting parameter. According to our previous publications and surface tension of EVA (24.7 mN/m at 200 °C) the wetting parameter is 8 and 0.72 for hydrophilic and hydrophobic silica, respectively. The same observation has been already done for other polymeric systems. However, the mechanism of migration of the particles to reach the equilibrium conditions in high viscous media is not still understood [8]. This will be investigated in further work.

As we previously underlined, the viscosity ratio between the two phases seems not to have significant influence on the final morphology. Moreover, interfacial tension between the two phases plays an important role in the establishment of the equilibrium size of the EVA droplets. However, its knowledge alone is not sufficient to explain why the size of the final morphology is quite the same whatever the initial viscosity ratio. Without silica, the blends have similar interfacial tension values but the characteristic size of the dispersed phase is really different. In the case of blends with silica and especially for hydrophilic silica, the effective interfacial tension (see calculation in the next section) is observed to not be dependent on the PP/EVA viscosity ratio. Consequently, the size of EVA droplets is thus driven by the rheological properties and/or operating conditions (shear and elongation flows) during the mixing process.

A droplet isolated in a matrix undergoes rupture when the hydrodynamic stress generated by the matrix overcomes the



-Morphology of PP/EVA03 80/20
-3 wt% SiN20 hydrophilic silica
-blending procedure 1

-Morphology of PP/EVA420 80/20 blend
-3 wt% SiN20 hydrophilic silica
-blending procedure 1

Fig. 3. Morphology of PP/EVA80/20 blend prepared with blending procedure 1 (the three components added simultaneously in the extruder). (a) PP/EVA03 with 3 wt% Si N20 hydrophilic silica. (b) PP/EVA420 with 3 wt% Si N20 hydrophilic silica.

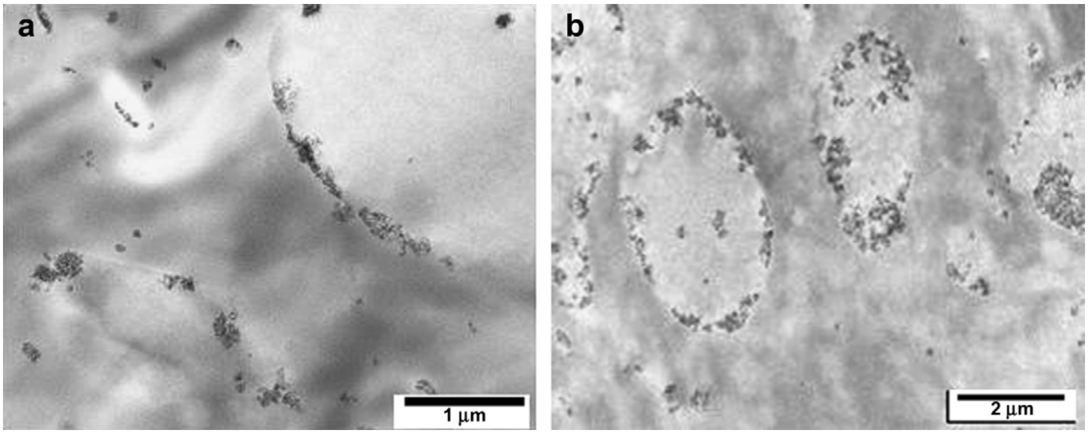


Fig. 4. Morphology of PP/EVA80/20 blends prepared with blending procedure 2 (the silica was pre-compounded with PP at 200 °C for 5 min. Then the obtained material was blended with the EVA28 03 during a second extrusion step). (a) PP/EVA420 80/20 blend filled with 3 wt% Si H20 hydrophobic silica. (b) PP/EVA420 80/20 blend filled with 3 wt% Si N20 hydrophilic silica.

cohesive stress of the droplet represented by the interfacial stress. This critical condition is given by the so-called capillary number C_a. When pure shear stress is applied on the system, the capillary number is very sensitive to the viscosity ratio [29]. The influence is less pronounced when pure elongational flow is applied. This is particularly true in the viscosity ratio range around unity where the capillary number seems to be almost constant whatever the viscosity ratio. From a rheological point of view, this could be one of the reasons why the final morphology is not dependent on the viscoelastic properties of both phases. However, due to the complexity of flow in an extruder, it is difficult to assert that the nature of the flow is responsible of the morphology obtained. Regarding the coalescence mechanism, silica particles prevent the coalescence rate and consequently promote droplet size reduction as the balance between break up and coalescence is shifted to the break-up mechanism.

3.2. Rheological behavior of PP/EVA/Silica nanocomposites

The rheological behavior of polymer blends is generally complex in the case of immiscible blends where the rheological properties depend strongly on composition and viscoelastic properties of the components. Palierne [30] developed a model that can predict the linear viscoelastic behavior of polymeric emulsions, taking into account the size of the viscoelastic droplets dispersed in a viscoelastic matrix and the interfacial tension between the components. However, the situation here is complicated by the presence of the nano-fillers.

Few years ago, we used the Palierne model [31,32] in the case of the crystallization from the melt at high super-cooling in finely dispersed polymer blends. The model was successfully adapted 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 Einstein's law in the same way as the expression of the complex shear moduli of filled system. In the presence of fumed silica, the Einstein law cannot be applied due to the fractal structure of these particles even at low concentration. Consequently, the Palierne model was addressed in a previous work [23] using the experimental viscoelastic data of respective filled components. Depending on silica nature, particular rheological cases have been investigated thanks to the partition of the silica between dispersed and matrix phases according to SEM and TEM observations. This method was used to calculate the ratio γ_{12}/R_v (interfacial tension over the volume average droplet radius) from the measurement of the droplet relaxation time in the low frequency domain of the dynamic viscosity. However, in some cases, the droplet relaxation time is too similar with the one of the matrices. The two peaks corresponding to each relaxation process are much convoluted and the determination of the relaxation times becomes inaccurate. Figs. 5 and 6 clearly point out such viscoelastic behavior of the blend.

In order to overcome this difficulty, we address in the present work an improved route to calculate the ratio γ_{12}/R_v using the rheological behavior of immiscible blend filled with solid particles. The ratio γ_{12}/R_v is accessible after isolating the droplet contribution to the complex relaxation modulus. Indeed, the Palierne model can be divided in two contributions according to the following equation.

$$G^*_{\text{Palierne}} = G^*_{\text{Composition}} + G^*_{\text{droplet}} \qquad (1)$$

where $G^*_{\text{Composition}}$ is the complex shear moduli of the blend without any interfacial effects. The Kerner model [33] is able to predict precisely such behavior. Actually, Kerner model corresponds to the Palierne model with interfacial tension set to zero.

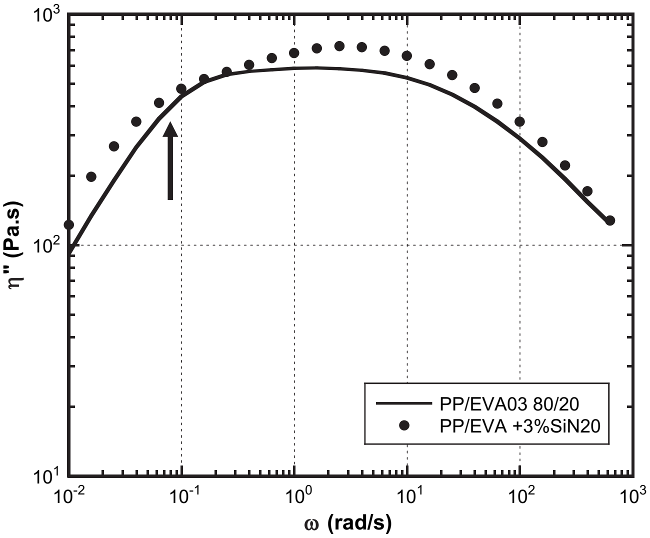


Fig. 5. Frequency dependence of η'' for PP/EVA03 blend filled with 3% silica particles. The silica particles have been simultaneously dispersed in PP/EVA03 blend during mixing. (●) Blend with hydrophilic silica (N20) and full line: experimental virgin blend. The arrow indicates the relaxation time of the EVA droplets.

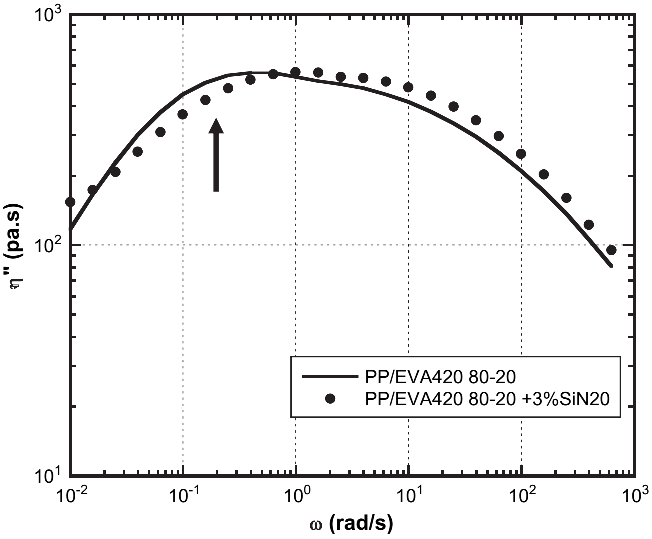


Fig. 6. Frequency dependence of η'' for PP/EVA420 blend filled with 3% silica particles. The silica particles have been simultaneously dispersed in PP/EVA420 blend during mixing. (●) Blend with hydrophilic silica (N20) and full line: experimental virgin blend. The arrow indicates the relaxation time of the EVA droplets.

G^*_{droplet} captures the interfacial effects and specially the extra elasticity brought by the droplet deformability. Furthermore, it is easily shown that the storage part of the complex shear modulus G' for a blend of two viscoelastic fluids can be expressed as follows:

$$\begin{aligned} G'_{\text{Palierne}}\left(\gamma_{12}, G^*_{\text{m}}, G^*_{\text{d}}\right) &= G'_{\text{Palierne}}\left(0, G^*_{\text{m}}, G^*_{\text{d}}\right) \\ &\quad + G'_{\text{Palierne}}(\gamma_{12}, \eta_{\text{m}}, \eta_{\text{d}}) \\ &= G'_{\text{Kerner}} + G'_{\text{Palierne}}(\gamma_{12}, \eta_{\text{m}}, \eta_{\text{d}}) \end{aligned} \qquad (2)$$

where G^*_{m}, G^*_{d}, are, respectively, the complex shear moduli of the matrix and the dispersed phase, η_{m}, η_{d} are, respectively, the Newtonian viscosity of the matrix and that of the dispersed phase.

In the previous equation, only the second term depends on the interfacial tension. This corresponds to the droplet contribution G^*_{droplet}. This part can be easily isolated.

The main idea of the method is to reveal the contribution of the relaxation of the droplets which depends on the interfacial tension γ_{12} by subtracting the composition effects to the experimental data of G^*. This implies obviously that Kerner's model correctly describes the polymer blend complex shear modulus. This is checked in the high frequencies zone for which the effect of droplet relaxation and then interfacial tension is negligible. Fig. 7 shows the very good agreement between the experimental curves and the Kerner law for frequencies above 2 rad s^{-1}. The parameters used in the model are not adjusted. Only measured data of $G^*{}_{\mathrm{PP}}$ and $G^*{}_{\mathrm{EVA}}$ have been used.

Moreover, the extra elasticity brought by the droplets deformation at low frequencies can be pointed out. So, this droplet contribution to the elastic modulus is obtained by subtracting the Kernel prediction to the experimental data of G': $G'_{\mathrm{droplet}}(\omega) = G'_{\mathrm{exp}}(\omega) - G'_{\mathrm{Kerner}}(\omega)$. Fig. 8 shows typical results.

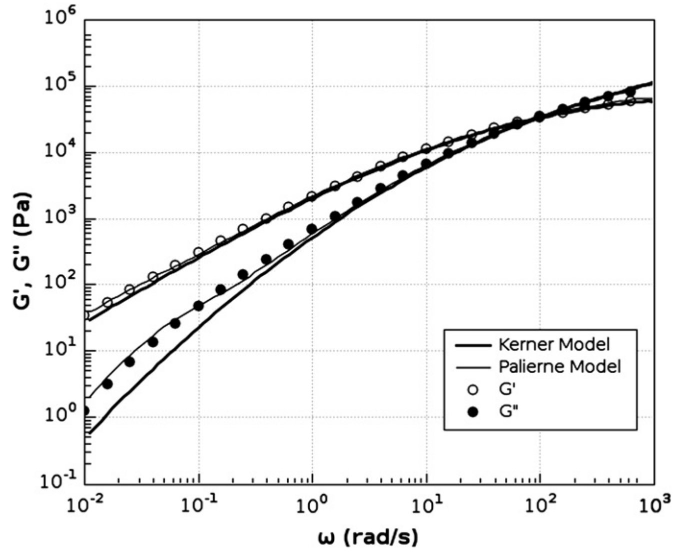


Fig. 7. Modeling of the viscoelastic behavior of PP/EVA03 80/20 with 3 wt% silica particles. The thick line represents the prediction from Kerner model, $T = 200\,^{\circ}\mathrm{C}$. The thin line corresponds to the Palierne model with $\gamma_{12}/R = 550$ Pa.

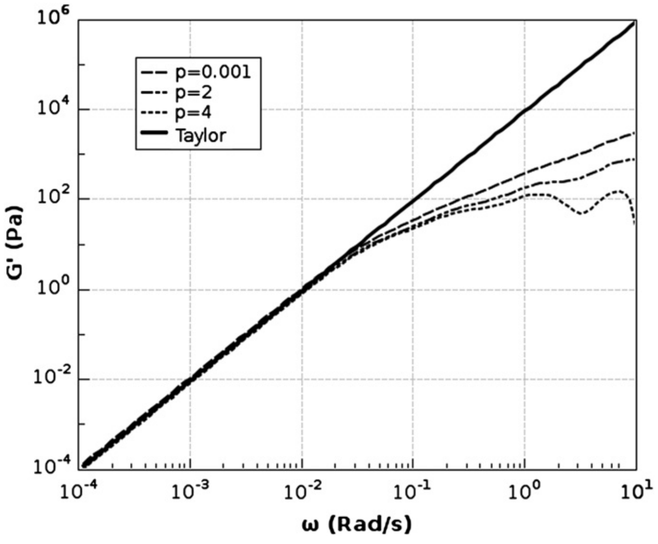


Fig. 8. Droplet contribution to the elastic modulus obtained by subtracting the Kernel prediction to the experimental data of G' for three different values of the viscosity ratio p. The solid line represents the modeling from Taylor model for blends of Newtonian liquids.

Obviously, the shape of the curve corresponding to the droplet relaxation in Fig. 8 does not match exactly with the expected one from Palierne model. One expects a plateau at high frequencies which is not clearly visible. Actually, the accuracy of the Kerner prediction in this frequency zone affects this plateau. Anyway, experimental accuracy does not allow us to observe it. Information from this plateau is not accessible. On the contrary, the lower frequency zone of the "extracted" droplet contribution is always clearly defined i.e. straight line with slope 2 in log–log scale is always observed. This linear increase of G' was already predicted by Taylor [28] who gives the following Eq. (3) showing that even a system composed by two immiscible Newtonian fluids can exhibit elasticity. This is the case in the terminal zone of the blend where both components are considered as Newtonian fluids.

$$G'_{\mathrm{Taylor}}(\omega) = \frac{\varphi\gamma_{12}\eta_{\mathrm{PP}}^2}{80R}\left(\frac{19p+16}{p+1}\right)^2\omega^2 \tag{3}$$

As the low frequencies zone is well defined, Eq. (3) can be then derived to determine the interfacial tension between PP and EVA. The droplet concentration φ or the zero shear viscosity η_{PP} is easily obtained. This is not the case for the viscosity ratio p which is extremely difficult to calculate precisely due to the fractal nature of the silica. Actually, the partition in both polymer phases is another parameter to take into account. However, the TEM observations allow us to assert that both hydrophilic and hydrophobic silica particles are located in EVA phase.

Consequently, two limit values of p corresponding to extreme limit behaviors have been used. The minimum value of p is related to the silica reinforcement of the EVA phase according to the Einstein law p_{min}: $p = \eta_{\mathrm{EVA}}(1+2.5\varphi)/\eta_{\mathrm{PP}}$. The maximum value is obtained if the fractal silica structure prevents the EVA droplet deformation: $p_{\mathrm{max}} \geq 4$. Note that percolation threshold for such silica particles in EVA matrix was observed to be closed to 3 vol% [34]. Thus, the corresponding limit values of $\gamma_{12}/R_{\mathrm{v}}$ define the uncertainties on the measure. In the present case, γ_{12} must be viewed as an effective interfacial tension [36], i.e. the free energy required to form a unit area of EVA surface covered with silica particles.

The values of the ratio $\gamma_{12}/R_{\mathrm{v}}$ and their uncertainties are obtained by fitting the straight line behavior on G' using Eq. (3). It is worth to note that in this range of viscosity ratio, the factor $(19p+16/p+1)^2$ as a weak influence on G' and the uncertainties on the ratio $\gamma_{12}/R_{\mathrm{v}}$ are consequently low.

According to this method, the effective interfacial tension of PP/EVA blend can be derived from the experimental measurement of R_{v}. Value of interfacial tension are reported in Table 2 for blends with or without silica particles. Without silica, the blends have quite similar interfacial tension values whatever the viscosity ratio. This value is close to this obtained ($\gamma_{12} = 1.2$ mN/m at 200 °C) using the harmonic mean established by Wu from the surface tension of the components.

Our results show that adding silica in the blends tends to decrease significantly the effective interfacial tension whatever the nature of the surface of the silica, hydrophobic or hydrophilic.

This result was already observed in the previous work on PP/PS blend only with hydrophilic silica which was preferentially located in the PS phase. In the present system, both silica cause the decrease of the effective interfacial tension of PP/EVA/silica blends. Taking into account the localization of the silica more than the nature of the silica surface, our results show that only when the silica particles are located in the dispersed phase, they cause the decrease of the effective interfacial tension.

However, the decrease of the effective interfacial tension due to the presence of silica particles in the volume of the dispersed droplets is difficult to understand. One explanation could arise from the thermodynamic origin of the interfacial tension.

From a thermodynamic point of view, interfacial tension is defined as $\alpha = \partial G/\partial A$ where G is the free enthalpy of the system and A is the interfacial area between the two phases. An increase in the interfacial area causes an increase in the free energy. The free energy can be viewed as the elastic energy stored by the droplet during its deformation.

Droplets with silica particles can be considered as a multiphase system. Droplet is divided into many sub-droplets whose surface is covered by silica particles. The sub-droplet is deformable and its surface tension depends on the quantity and the structure of the silica particles on its surface. This has been already shown in oil/water emulsions in which nanoparticles were introduced [35,4]. The presence of silica at the interface between the phases causes a decrease of the “effective interfacial tension”. The amplitude of the interfacial tension reduction depends on the quantity of particles at the surface of the droplets.

As all the sub-droplets i are deformable, their surface area A_i are changing when the surface area of the whole droplet A_d is changing. Each sub-droplet generates its own increase in free energy due to its own interfacial tension and surface. The contribution ΔG_i of the sub-droplet i is given by: $\Delta G_i = \gamma_{12_i}\Delta A_i$.

As already shown for multilayer systems [36], the whole free energy change ΔG_d is then given by the sum of each contribution:

$$\Delta G_d = \sum_i \Delta G_i = \sum_i \gamma_{12_i}\Delta A_i \tag{4}$$

The interfacial tension of the whole droplet is thus calculated from the variation of the free energy of the droplet divided by the variation of its surface as follows:

$$\langle\gamma_{12}\rangle = \frac{\Delta G_d}{\Delta A_d} = \frac{\sum_i \gamma_{12_i}\Delta A_i}{\Delta A_d} \tag{5}$$

Then interfacial tension of such multiphase systems can be considered as an average value derived from the distribution of particles in the volume of the droplet. Not only intrinsic value of the silica surface tension must be taken into account but also how the silica is structured into the droplet.

It is then clear that, the addition of silica in polymer blend modifies both rheological and thermodynamic behaviors of the system. The presence of silica particles in the EVA droplets tends to decrease the interfacial tension and then causes a significant reduction of the droplets size. Vignati et al. who studied oil/water emulsions considered that interfacial tension does not play a large role in the stabilization mechanism but it is difficult to generalize their conclusions to our system since the difference of surface tension between silica and PP or EVA is larger than silica and water. However, the presence of particles at the interface can alter its mobility and consequently may induce “rheologically” decrease of interfacial tension. This is unambiguously impossible for hydrophilic silica which is preferentially located in the droplet core and seems to avoid the interface. By contrast, for hydrophobic silica which locates closer to the interface, pure surface rheological effects are possible but harder to estimate. Furthermore, many other parameters such as the nature (shear and elongation) of the flow, the fractal structure of the silica in dispersed phase modifying its viscoelastic behavior, steric hindrance of droplets coalescence may have an impact on the final morphology and it is still difficult to discriminate between all of them.

4. Conclusion

The effect of two types of fumed silica (hydrophilic and hydrophobic) on the morphology of PP/EVA80/20 blends was investigated.

- First of all, a significant reduction of the EVA droplets size was observed in the presence of both types of silica. Typically, the volume droplet radius decreases from 2.2 μm to nearly 0.5 μm for filled blends with 3 wt% silica.
- SEM and TEM image analyses proved that the hydrophilic silica tends to confine in the EVA phase whereas hydrophobic one was located close to the PP/EVA interface in the EVA. For the latter case, no clear interphase of PP/Silica/EVA has been observed.
- With the blending procedure consisting in pre-blending silica particles in PP matrix, a migration of hydrophilic silica from PP phase toward 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. Based on this model, an improved method of determination of the effective interfacial tension from rheological measurement has been addressed. When the relaxation of the droplet is not sufficiently separated from the whole blend relaxation, the method allows to express the droplet contribution to the elastic modulus. The effective interfacial tension values are then easily determined with an improved accuracy. A decrease of this effective interfacial tension was again observed for both silica whatever the viscosity of the EVA droplet. It seems that silica plays a thermodynamic role in the stabilization mechanism especially in the case of hydrophilic silica. Silica induces a decrease in the effective interfacial tension which tends to reduce the dispersed phase size. However, the interfacial tension alone is not able to explain this effect. The influence of particular rheological conditions and the structure of the phases must be taken into account but are still difficult to quantify for a complete understanding and prediction of the final morphology of such systems.

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