Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 6029–6040
polymer
www.elsevier.com/locate/polymer

Morphology and rheology of immiscible polymer blends filled with silica nanoparticles

L. Elias [a,b], F. Fenouillot [c], J.C. Majeste [d], Ph. Cassagnau [a,b,*]

[a] *Université de Lyon 1, Université de Lyon, Lyon F-69003, France*
[b] *CNRS UMR5223, Ingénierie des Matériaux Polymères—Laboratoire des Matériaux Polymères et Biomatériaux, F-69622 Villeurbanne, France*
[c] *Ingénierie des Matériaux Polymères—Laboratoire des Matériaux Macromoléculaires (IMP/LMM), UMR-CNRS 5223, INSA-Lyon, 17 Avenue Jean Capelle, 69621 Villeurbanne Cedex, France*
[d] *Ingénierie des Matériaux Polymères—Laboratoire de Rhéologie des Matières Plastiques (IMP/LRMP), UMR-CNRS 5223, Université Jean Monnet, 23 rue du docteur Paul Michelon, 42023 Saint Etienne Cedex 2, France*

Received 10 May 2007; received in revised form 22 June 2007; accepted 26 July 2007

Abstract

The effect of silica nanoparticles on the morphology and the rheological properties of an immiscible polymer blend (polypropylene/polystyrene, PP/PS 70/30) was investigated. Two types of pyrogenic nanosilica were used: a hydrophilic silica with a specific surface area of 200 m^2/g and a hydrophobic silica having a specific surface area of 150 m^2/g. First, a significant reduction in the PS droplet volume radius, from 3.25 to nearly 1 μm for filled blends with 3 wt% silica, was observed. More interestingly, image analysis of the micrographs proved that the hydrophilic silica tends to confine in the PS phase whereas hydrophobic one was located in the PP phase and at the PP/PS interface (interphase thickness ≈ 100–200 nm). Furthermore, a migration of hydrophilic silica from PP phase toward PS domains was observed.

An 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 the viscosity ratio, limited cases have been investigated. The rheological data obtained with the hydrophobic silica were more difficult to model since the existence of a thick interphase cannot be taken into account by the model. Finally, the hypothesis that hydrophilic silica is homogeneously dispersed in PS droplets and that hydrophobic silica is dispersed in PP matrix was much closer to the actual situation. It can be then concluded that stabilization mechanism of PP/PS blend by hydrophilic silica is the reduction in the interfacial tension whereas hydrophobic silica acts as a rigid layer preventing the coalescence of PS droplets.

Keywords: Silica; Blends; Linear viscoelasticity

1. Introduction

One of the challenges in formulating new polymeric blends is to predict how additives will affect the overall phase behaviour and performance of the material, especially when these polymers are immiscible and their blending leads to materials with weak interfacial adhesion and thus poor mechanical performances. One of the classical methods to ensure adhesion between the phases (reduction in the interfacial tension) is the use of a third component, a compatibilizer, which is usually a macromolecule designed to manipulate the interfacial properties. Such a macromolecule, generally a block copolymer, refines the droplet size of the dispersed minor phase, stabilizes it against coalescence during melt mixing and ensures strong interfacial adhesion between the phases. This classical compatibilization strategy has been widely used to produce a variety of industrial polymer blends.

In recent years, a new concept of compatibilization by using inorganic nanoparticles has been introduced. This idea is

---

* Corresponding author. Université de Lyon 1, Université de Lyon, Lyon F-69003, France. Tel.: +33 4 72446208; fax: +33 4 72431249.
E-mail address: philippe.cassagnau@univ-lyon1.fr (Ph. Cassagnau).

0032-3861/$ - see front matter
doi:10.1016/j.polymer.2007.07.061

of scientific importance, and possesses a profound prospect in industrial application. Actually, there are relatively few studies dealing with immiscible polymer blends whose interfaces are stabilized by solid particles; while studies on low viscosity emulsions have been extensively reported. One century ago, Ramsden [1] and Pickering [2] observed that the emulsion stability can be efficiently promoted by dispersed colloidal particle. Note that these types of emulsions are generally named Pickering emulsions according to these original works. More recently, Tambe and Sharma [3] observed that the stability to coalescence of decane-in-water emulsion increased as the particle concentration of calcium carbonate particles was raised. On the other hand, the research group of Binks [4–9] have extensively studied the stabilization and the phase inversion of water–oil emulsion by nanosilica particles. They have shown that the emulsion of water-in-oil was completely stable to coalescence as a result of an adsorbed layer of particles at the oil–water interface. As the silica particle concentration in the emulsion is increased, the average drop diameter decreases until a minimum size is reached due to the fact the coalescence process during drop formation is reduced. Furthermore, the role of the surface chemistry of silica particles and the type and composition of the oil and aqueous phases in improving the stability of these low viscosity emulsions have been also reported. For example, more hydrophobic particles stabilize only water/oil emulsion whereas more hydrophilic one stabilizes only oil/water emulsions. Interestingly, Vignati and Piazza [10] showed that the interfacial tension is not modified by particle adsorption at the interface, suggesting steric hindrance or surface rheology effects as the most probable stabilization mechanism.

Regarding high viscous emulsions, i.e. immiscible polymer blends, the use of organically modified silicate as a nanofiller and as a compatibilizer at the same time has been recently established [11–15]. Generally speaking, these 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. However, Hong et al. [16,17] 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/clay system. Furthermore, the presence of organoclay at the interface hydrodynamically stabilizes the blend morphology by preventing the coalescence of the droplets making this morphology thermo-mechanically stable.

Actually, the influence of fillers on blend morphologies has been already reported far before the organoclay fashion. Maiti et al. [18] studied the distribution of carbon black (CB) and silica in nitrile rubber/epoxidized natural rubber (ENR) blends. They found that silica nanoparticles migrated preferentially to the ENR phase. It was believed that the reasons for the preferential migration of silica to ENR phase included the low viscosity of the ENR and a physical interaction between the epoxide group of ENR and the silanol group of silica. Gubbels et al. [19] studied the kinetic and the thermodynamic control of the selective localization of CB at the interface of polyethylene (PE)/polystyrene (PS) blends. They showed that the stability of the polymer morphology is remarkably improved when the CB particles occupy the interfacial region. Clarke et al. [20] showed that the CB has a powerful compatibilizing effect when present at the interface between natural rubber (NR) and nitrile butadiene rubber (NBR). The compatibilizing effect of nanosized calcium carbonate filler was studied [21] on immiscible blends of styrene-*co*-acrylonitrile/ethylene propylene diene (SAN/EPDM). The results suggest that the morphology of the SAN/EPDM blends is affected through the reduction in surface energy of the filler. On the other hand, Zhang et al. [22] showed that the compatibility of PP/PS blends can be considerably improved with the addition of nanosilica particles. The silica concentration and mixing time also have a significant effect on this compatibility. However, no any quantitative calculation of the influence of silica on the size reduction in PS droplets has been addressed in this work. Finally, Thareja and Velankar [23] showed more recently that the addition of fumed silica in PIB/PDMS blends can induce clustering of the drops and consequently the blends appear to show gel-like behaviour.

Actually, the mechanisms by which particles stabilize against coalescence are not completely understood in polymeric emulsions. However, Vermant et al. [24] investigated the effect of nanometer sized silica on the flow-induced morphology of models of immiscible polymer blends. The effect of pre-shear rate and particle concentration on the blend morphology was studied and the ratio of the droplet radius over the interfacial tension (R/γ_{12}) was derived assuming a quasi-Maxwellian behaviour of the rheological properties of this polymeric emulsion. They concluded that the phenomena observed are similar to those observed in low viscosity emulsion (so called Pickering emulsions).

In the present work, we investigate the effect of silica nanoparticles on the morphology and the rheological properties of immiscible polymer blend (PP/PS) with the help of the Palierne model [25] as the general framework of this quantitative study. The use of pyrogenic nano-SiO_2 particles was 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, nanosilica particles are used as filler in various industrial applications to control the rheological properties.

2. Experimental part

2.1. Materials

PP was supplied by Atofina (PPH 7060) with a melt flow index MFI = 12 g/10 min. The molecular weights are: $\overline{M}_n = 67,300\ \mathrm{g\,mol^{-1}}$ and $\overline{M}_w = 273,000\ \mathrm{g\,mol^{-1}}$. The PS was kindly supplied by Arkema (Lacqrene Cristal PS 1960 N) with $\overline{M}_n = 49,300\ \mathrm{g\,mol^{-1}}$ and $\overline{M}_w = 93,500\ \mathrm{g\,mol^{-1}}$. Fig. 1 shows the variations of the complex shear modulus ($G^*(\omega) = G'(\omega) + jG''(\omega)$) of these two polymers at the temperature $T = 200$ °C. The zero shear viscosity (η_0) of PP and PS is then 2500 and 1000 Pa s, respectively. The silica content

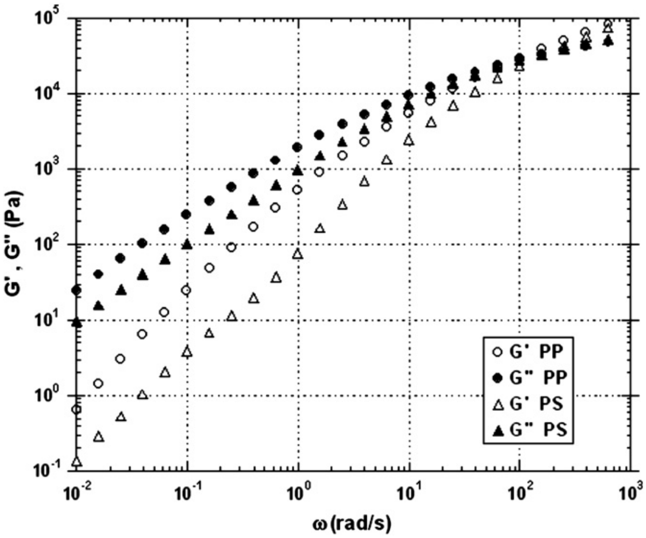

Fig. 1. Viscoelastic behaviour of PP and PS at $T = 200$ °C.

was 3 and 6 wt% of the total material and the proportion of PS in PP was always 30 wt%.

Two types of nanosilica (SiO_2) were used: a hydrophilic pyrogenic silica, Aerosil A200, with a specific surface area of 200 m^2/g and a hydrophobic nanosilica, Aerosil® R805, having a specific surface area of 150 m^2/g and 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 supplied by Degussa 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 were loaded to the mixing chamber simultaneously and compounded at 200 °C for 5 min.
(2) The silica was pre-compounded with either PP or PS at 200 °C for 5 min. Then the obtained material (PP/silica or PS/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 $0.01 < \omega$ ($rad\,s^{-1}$) < 628. All experiments were performed in the domain of the linear viscoelasticity and under nitrogen atmosphere in order to prevent thermo-oxidative degradation.

First of all, a degradation of the PP matrix (chain scission) was observed by rheology (Fig. 2a) when the hydrophilic silica (A200) was dispersed in the extruder under air atmosphere. This result was confirmed by size exclusion chromatography (see Fig. 2b) which proved that molecular weight decreases from $\overline{M}_w = 273,000\ g\,mol^{-1}$ for neat PP to $\overline{M}_w = 202,500\ g\,mol^{-1}$ for PP filled with fumed silica and extruder under air atmosphere.

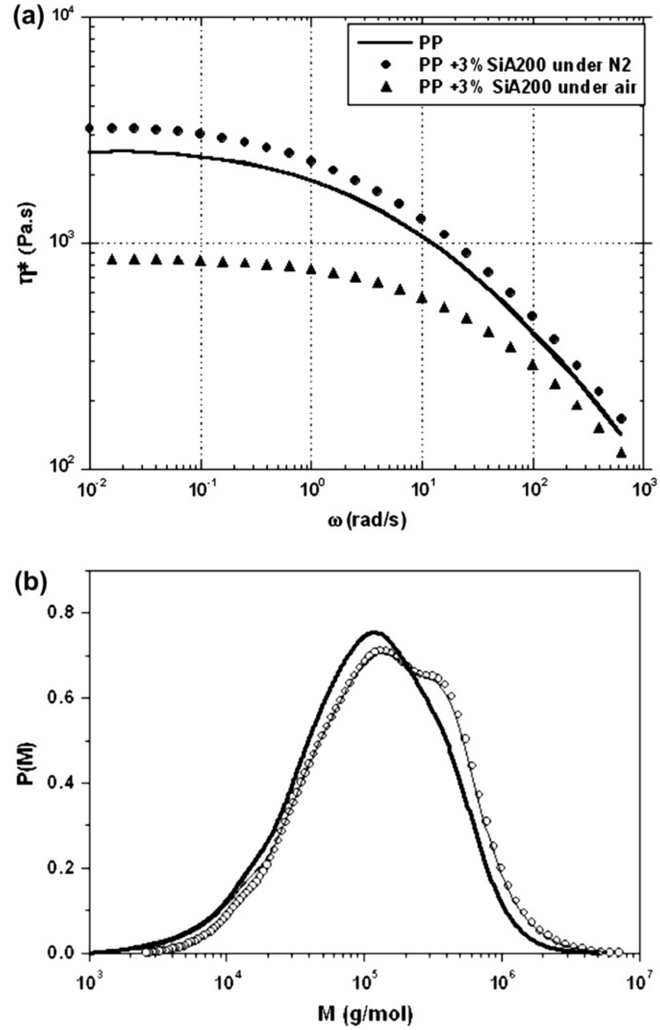

Fig. 2. Influence of processing conditions under air or nitrogen atmosphere on the PP/silica degradation. (a) The complex shear viscosity is measured at 200 °C (under nitrogen in the rheometer oven) after having processed PP alone under air and PP + 3% silica under air and under nitrogen. (b) Corresponding molecular weight distribution of (a). Symbols: neat PP, thin full line: PP + 3% silica under nitrogen, thick full line: PP + 3% silica under air.

Our results could explain the rheological behaviour of Zhang et al. [22] who also observed a viscosity decrease in silica filled PP. By contrast, we observed that hydrophobic silica (R805) did not degrade the PP matrix under the same conditions of mixing. The PS polymer was stable whatever the processing conditions and the silica nature. The origin of this phenomenon of degradation could be attributed to the interactions between PP oxidative stabilizers and Si–OH groups at the surface of hydrophilic silica which leads to decrease in the thermal stabilizer concentration in PP bulk. This oxidative degradation can be prevented by adding more stabilizers or by compounding the composite under nitrogen atmosphere. The last-mentioned solution was used in all experiments.

2.3. Morphology characterization

The morphology of the materials was observed by scanning electron microscopy (SEM) using a Hitachi S800 model. The samples were fractured in liquid nitrogen. The PS phase was selectively extracted by tertrahydrofuran (THF) solvent at room temperature to enhance the contrast. The fractured surfaces were sputter-coated with gold/palladium (50/50). Furthermore, 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 observed using a Philips CM120 transmission electron microscope.

The droplet size was determined by using image analysis. The radius 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–Saltikov [26] method. The correction was done by first dividing the particle size into 15 linear size ranges and by characterizing each size range with midpoint of the range. The particle size was then multiplied by a matrix of coefficients resulting from a set of equations to get the real particle size distribution in three dimensions.

The number average radius (R_n) and the volume average radius (R_v) were calculated based on the real particle size distribution by Eqs. (1) and (2), respectively:

$$R_n = \frac{\sum_i (N_v)_i R_i}{\sum_i (N_v)_i} \tag{1}$$

$$R_v = \frac{\sum_i (N_v)_i R_i^4}{\sum_i (N_v)_i R_i^3} \tag{2}$$

with $(N_v)_i$ as the number of particles having radius R_i. Finally, the size polydispersity d was characterized by $d = R_v/R_n$.

3. Results and discussion

3.1. PP/silica and PS/silica nanocomposites

Since the interaction between the polymer components and the filler plays an important role in determining the phase separation behaviour and final morphology, it is important to determine the effect of silica nanoparticles on the viscoelastic behaviour of respective homopolymer composites. For this purpose, composites with different concentrations of silica particles were prepared. PP and PS were mixed with 3, 6, and 10 wt% of hydrophilic silica (A200) corresponding to 1.35, 2.70 and 4.50 v%, respectively.

It is now well admitted that particle-filled molten polymers present a sol–gel (also named liquid–solid) transition due to the formation of a gel-like structure by solid particles. This gel behaviour is characterized by the appearance of a constant elastic modulus at low frequencies corresponding to a yield stress behaviour of the viscosity. Fig. 3a and b shows that these silica composite polymers exhibit a gel-like behaviour or more precisely a yield stress behaviour for silica concentration beyond 6 wt% (2.7 v%). This result agrees well with the order of magnitude already reported for polymer filled with silica particles. Cassagnau [27] observed a silica volume content of $\Phi_c = (3.3 \pm 0.1) \times 10^{-2}$ for the onset of a gel-like behaviour in the terminal zone and Inoubli et al. [28] estimated that 2.5 v% of silica was very close to the percolation threshold. In the present work, this result is of importance to select the silica concentration for the rheological modelling purpose. Actually, silica concentration above the percolation threshold could block out the relaxation mechanisms of dispersed droplets. In other words, the silica concentration must be strictly lower than that of the percolation threshold in order to be

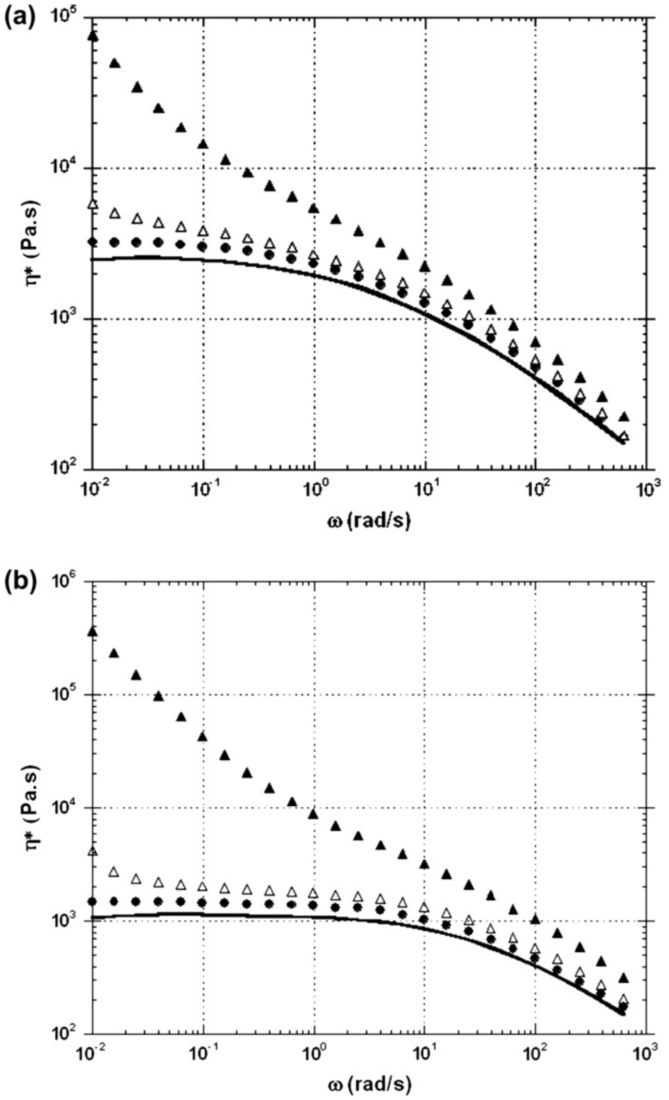

Fig. 3. Variation of the complex shear viscosity of PP and PS composites filled with different silica concentrations. $T = 200$ °C. (a) PP and PP/silica and (b) PS and PS/silica. The full lines are for the neat polymers, (●) 3 wt% silica, (△) 6 wt% silica (▲) 10 wt% silica.

able to successfully apply the Palierne model. Consequently, the silica concentration was fixed at 3 wt% (1.35 v%).

3.2. Blends morphology of PP/PS/silica nanocomposites

The objective here is to investigate how the presence of the silica and its localization in the biphasic blend influences the morphology. At the equilibrium, the localization of the silica particles is governed by thermodynamics. Silica particles can be distributed nonhomogeneously. Two situations are distinguished: (i) the particles are distributed mainly and homogeneously in one of the two phases and (ii) the particles are confined at the interface between the two polymers. This distribution can be predicted qualitatively by comparing surface tension of the three components. Difference between interfacial tensions imposes the place where the silica will be localized after stopping the mixing. This place can be predicted using a wetting parameter ω, defined as follows:

$$\omega_1 = \frac{\gamma_{\mathrm{Si}-2} - \gamma_{\mathrm{Si}-1}}{\gamma_{12}} \tag{3}$$

where $\gamma_{\mathrm{Si}-i}$ is the interfacial tension between the silica particle and the polymer i and γ_{12} is the interfacial tension between the two polymers.

When $\omega_1 > 1$ the silica is present only in polymer 1. For value of $\omega_1 < -1$ the particles are only found in polymer 2. For other values of ω_1, the silica is concentrated at the interface between the two polymers.

Estimation of the interfacial tension between two components 1 and 2 is achieved using the well-known Owens and Wendt [29] equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^{\mathrm{d}}\gamma_2^{\mathrm{d}}} - 2\sqrt{\gamma_1^{\mathrm{p}}\gamma_2^{\mathrm{p}}} \tag{4}$$

where the exponents d and p stand for, respectively, the dispersive and the polar contributions to the surface tension. The blends have been prepared at 200 °C. As surface tension is temperature dependent, a way to estimate γ at other temperature is the application of a relationship found by Guggenheim [30]:

$$\gamma = \gamma(0)(1 - T/T_{\mathrm{cr}})^{11/9} \tag{5}$$

The values of $\gamma(0)$ and T_{cr} are given in Table 1. Eq. (5) shows that surface tension decreases with temperature. The calculation of the interfacial tension requires to know the values of the polar and dispersive contribution to the surface tension. These are commonly given in the literature at room temperature. Assuming that temperature dependence of each contribution follows the same law as for the surface tension, it is then possible to use Eq. (5) to estimate γ^{d} and γ^{p} at the temperature of mixing. For silica particles, the surface tension was estimated at 200 °C using the rate $\mathrm{d}\gamma/\mathrm{d}T$ which is assumed to be constant in the interval of temperature used.

For this system, at the temperature $T = 200$ °C, we found $\omega_{\mathrm{PS}} = 4.87$ for the hydrophilic silica particles and $\omega_{\mathrm{PS}} = -1.13$ for the hydrophobic one. At thermodynamic equilibrium, the hydrophilic silica particles should be preferentially located in the PS phase while the hydrophobic ones should be found at the interface and in PP. Note that in molten polymers, the thermodynamic equilibrium may be difficult to attain and the kinetic effects may dominate if the viscosity is high and/or the processing time is short. In other words, the morphology observed after a given mixing time may differ from that at the equilibrium since the particles migrate slowly toward their preferred phase.

Table 1
Surface tension data of the components of the blends

	Surface tension at 25 °C (mN/m)			$\gamma(0)$ (mN/m)	T_{cr} (K)	$\mathrm{d}\gamma/\mathrm{d}T$ ((mN/m)/K)
	γ	γ^{d}	γ^{p}			
PP	30.1	30.1	0	47.2	914	–
PS	40.7	34.5	6.1	63.3	967	–
R805 hydrophobic silica	32	30	2			−0.1
A200 hydrophilic silica	80	29.4	50.6	–	–	−0.1

First of all, the presence of silica particles reduces significantly the coalescence phenomena and the PS domain size is decreased by a factor three approximately as observed by comparing the micrographs (a) and (b) in Figs 4 and 5. More quantitatively, Fig. 6 shows the size distribution of PS drops and Table 2 their average radius. Clearly, silica particles are efficient at producing a relatively uniform distribution of drop sizes and the distribution shifts to smaller diameter.

The stabilization of emulsion by colloidal particles is known to proceed from at least two mechanisms: (i) the dense layer of solid particles prevents coalescence (ii) the viscosity of the continuous phase increases making the drainage of the thin film separating two droplets more difficult. In the latter case, the percolation of the particles in the matrix can further intensify the effect (for concentration above the percolation threshold). It is therefore important to determine how the silica particles are dispersed in the blend. Here, different situations are encountered. When the three components are added at the same time in the extruder (blending procedure 1), the hydrophilic A200 silica is found essentially in the PS droplets and also, to a less extent, at the interface (Fig. 4c–e). This corresponds well with the prediction based on the calculation of the surface tensions. On the other hand, the hydrophobic R805 silica is localized exclusively in the PP matrix and at the interface where a layer of particles is formed and is nicely visible in the images (Fig. 5c, e, and f). More precisely, TEM images (Fig. 5f) show that silica particles form an interphase layer of approximately 100–200 nm thick. Silica particles are not visible in the PS domains. Again, these features agree with calculations presented in Table 1.

When the hydrophilic A200 silica is mixed with PP first and subsequently mixed with PS (blending procedure 2) the silica particles initially dispersed in PP appear to be confined in the PS phase as predicted by the approximate estimation of

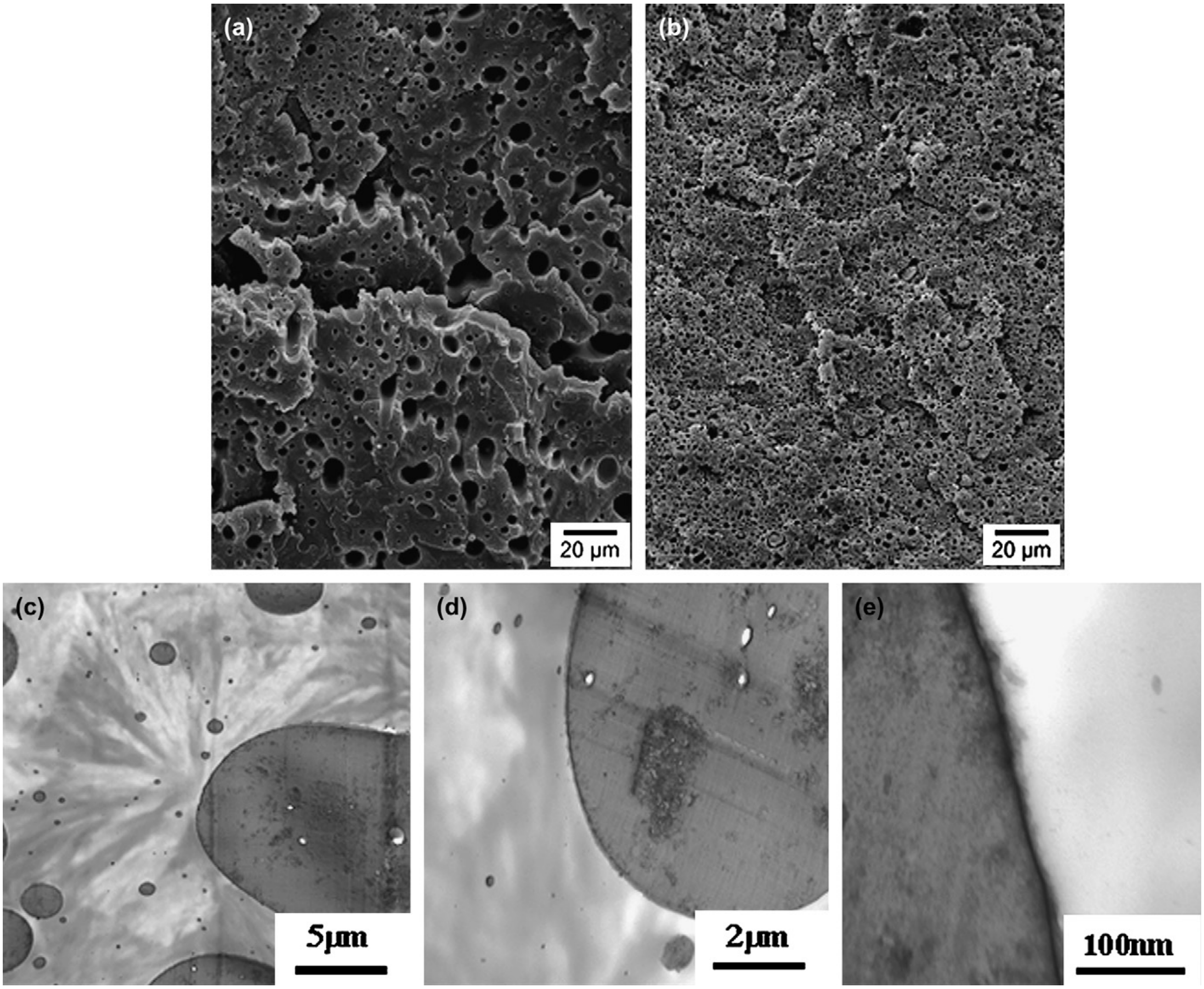

Fig. 4. Morphology of PP/PS 70/30 blend prepared with blending procedure 1 (the three components added simultaneously in the extruder). (a) PP/PS blend without silica, (b) blend filled with 3 wt% A200 hydrophilic silica, (c)−(e) are TEM images showing the confinement of the hydrophilic silica in the PS droplets and some silica at the interface.

the surface tensions and wetting parameter (Fig. 7). Interestingly, the silica particles have migrated from the PP phase toward the PS phase in which the interactions are more favourable. Actually, few authors report the same observation in polymers and currently the mechanism of migration of the particles is not well understood [19]. In this case, we can hypothesize that the system has reached the thermodynamic equilibrium and since the morphology is identical (qualitatively and quantitatively) to the one observed with blending procedure 1, we can conclude that the equilibrium was also reached with procedure 1.

If we come back to the aspect of the compatibilizing effect of the silica, our observation of the localization of the silica leads to several remarks. An important point is that the efficiency of the silica does not depend much on the nature of the silica and its ''final'' localization in the blend. Clearly the PS domains' size is strongly reduced compared to the PP/PS blend whatever the silica nature and the mode of addition of the silica (blending procedure 1 or 2). Thus it is difficult to determine which one of the stabilization mechanisms cited above (dense layer of solid particles at the interface, increase of the viscosity of the continuous phase) is responsible for the reduction in the coalescence. By ''final'' localization we mean the one that we observe after the blending procedure and it must be emphasized that during the course of the blending operation, the material does not reach the equilibrium immediately. Actually, silica particles are continuously moving in the velocity field and after a certain time their preferred localization is dictated by the equilibrium between hydrodynamic forces (shear) and thermodynamics (interactions). This means that several mechanisms limiting coalescence may be involved depending on the time of mixing. For instance, the hydrophilic silica seems to be slightly more efficient than the hydrophobic one to decrease the size of the PS domains. At the equilibrium, this silica is confined in the PS so that the concentration of silica in this phase is

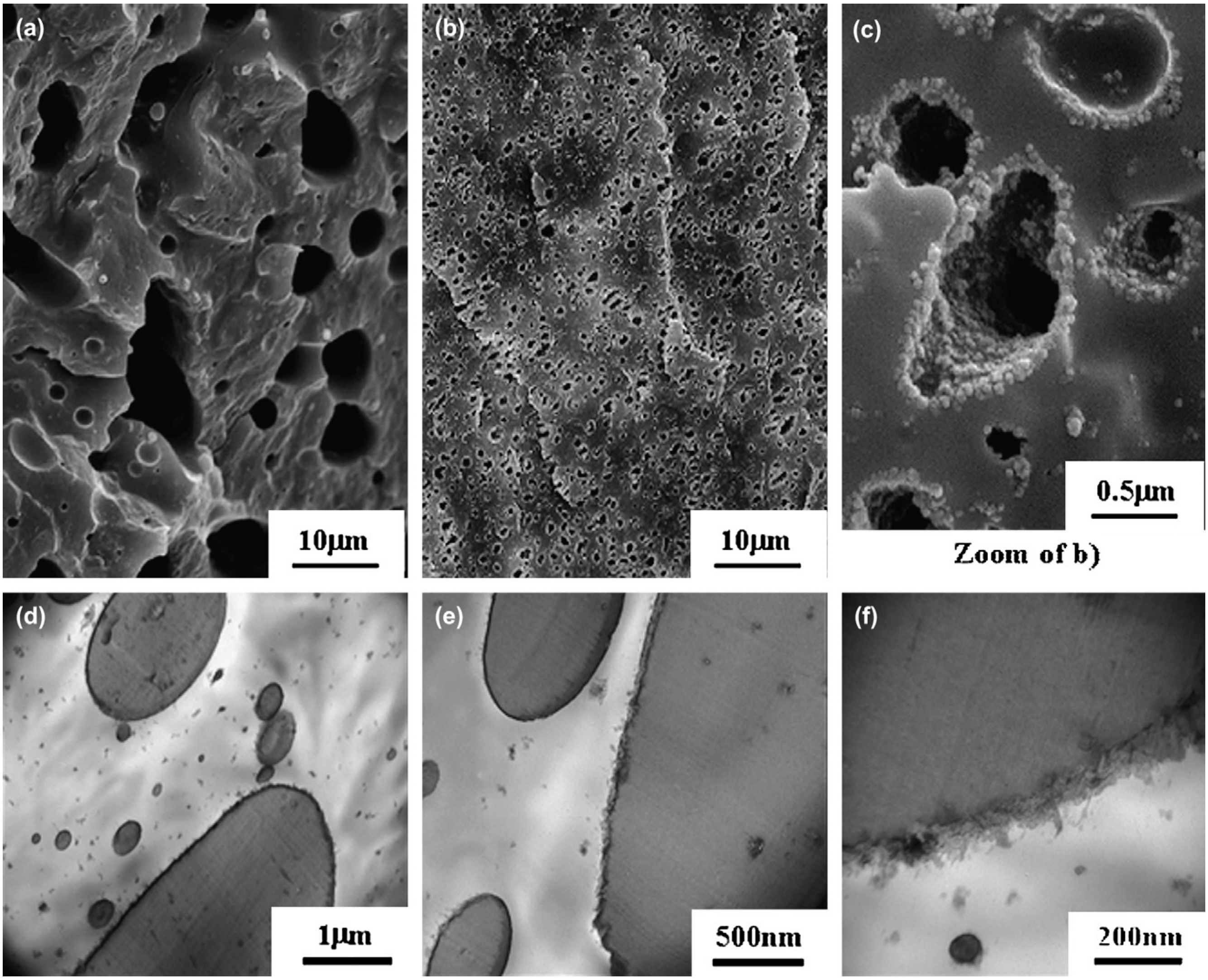

Fig. 5. Morphology of PP/PS 70/30 blend prepared with blending procedure 1 (the three components added simultaneously in the extruder). (a) PP/PS blend without silica, (b) blend filled with 3 wt% R805 hydrophobic silica, (c) zoom of image (b) and (d)–(f) are TEM images showing the hydrophobic silica in the PP matrix and located at the PP/PS interface.

close to 10 wt% if we consider that no silica is present in the PP (as can be seen in the images). This high concentration of silica in the PS droplets means that the liquid–solid transition is overcome and that PS droplets are highly viscous.

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 (Fig. 8a). 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 [31,32]. In a straightforward and simplest manner, the variation of $\eta''(\omega)$ describes qualitatively the relaxation spectra of the blend. As shown in Fig. 8b, a pronounced relaxation peak, reflecting the shape relaxation of the droplets, is clearly seen in the domain of low frequencies. The relaxation time, τ_s, calculated to be $1/\omega$ at the peak of the relaxation spectrum, is close to $\tau_s \approx 9$ s. Furthermore, since the emulsion model of Palierne [25] has been successfully applied in the past to obtain morphological and interfacial information on immiscible blends, we have used it to calculate the ratio γ_{12}/R_v (interfacial tension over the volume average droplet radius) from the best fit of the experimental and calculated dynamic moduli (see Fig. 8). Following this, the interfacial tension of PP/PS blend can be derived as R_v and has been measured with the help of the morphology pictures. We finally found $\gamma_{12} \approx 2.15$ mN/m. In order to confirm this result, the interfacial tension was also optically measured from a deformed drop retraction experiment. For further details on this method see Deyrail et al. [33] as for example. This method yields $\gamma_{12} \approx 2.50$ mN/m. Actually, this value is approximately twice lower than the value generally reported in the literature. Depending on

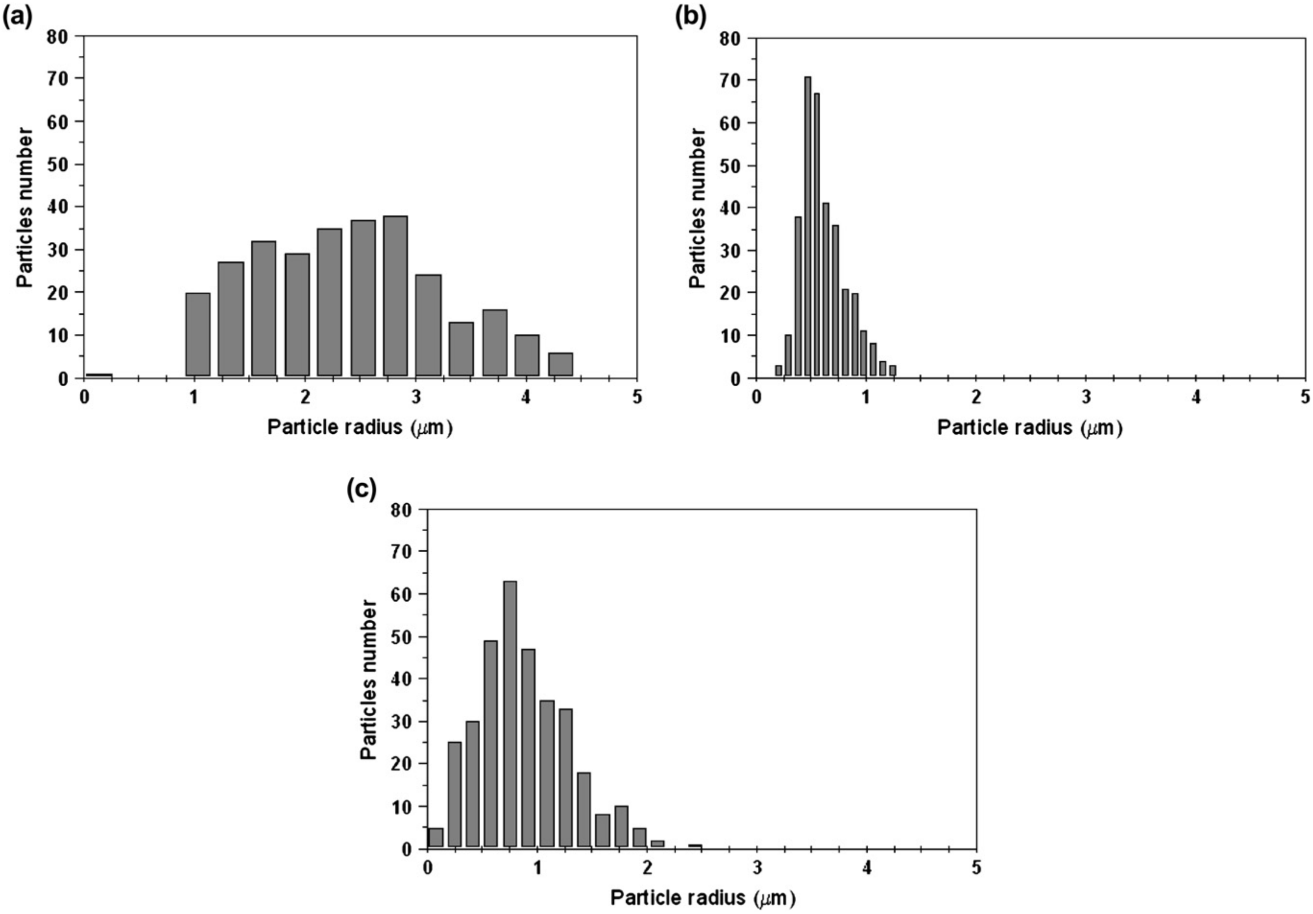

Fig. 6. Number distributions of the PS droplets radii in PP/PS (70/30) blends. (a) Virgin blend, (b) blend filled with 3 wt% hydrophilic silica (A200) and (c) blend filled with 3 wt% hydrophobic silica (R805).

Table 2
Average radius (R_v and R_n) of PS droplets in PP matrix

PP/PS 70/30		R_V (μm)	R_n (μm)	γ_{12}/R_v (mN/m^2)	γ_{12} (mN/m)
Without silica		3.25	2.40	660	2.15
A200 hydrophilic silica	Case 1: homogeneous dispersion	0.85	0.60	1000	0.85
	Case 2: total partition in PS	0.85	0.60	100	0.085
R805 hydrophobic silica	Case 1: homogeneous dispersion	1.25	0.80	1850	2.3
	Case 2: total partition in PS (10 wt%)	1.25	0.80	350	0.45
	Case 3: total Partition in PP (4.2 wt%)	1.25	0.80	2500	3.10

Composite blends have been filled with 3 wt% silica. The ratio γ_{12}/R_v was calculated from the Palierne model. γ_{12} is the interfacial tension calculated from γ_{12}/R_v values.

polymer molar mass and temperature, the reported values for interfacial tension between PP and PS range from 4 to 7 mN/m [32,34,35]. 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. [32], the values of γ_{12}/R_v are generally used in order to avoid any ambiguity with the interfacial tension. In the present study, we find $\gamma_{12}/R_v \approx 660$ mN/m^2 for neat PP/PS.

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. When 3 wt% of silica (hydrophilic or hydrophobic) is added in the blend with procedure 1, Fig. 9 shows that the relaxation of the PS droplets is shifted to lower relaxation times compared with the neat PP/PS blend ($\tau_s \approx 5$ s) (Fig. 10). In other words, the faster drop relaxation qualitatively means [25] that the interfacial forces increase when silica fillers have been added in

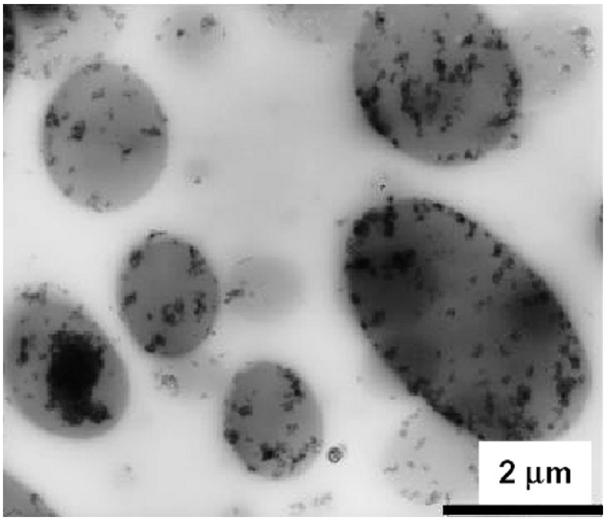

Fig. 7. TEM image of PP/PS/3 wt% A200 hydrophilic silica obtained with blending procedure 2 (premixing the silica with PP). The dispersed PS phase appears in grey and the silica in black. TEM was performed on thin film of 90 nm thickness.

the blend. Now if we compare blending procedure 1 (mixing PP, PS and silica simultaneously) with blending procedure 2 (silica pre-mixed in PP phase) we note in Fig. 10 that these two methods yield similar experimental rheological behaviours for blends filled with hydrophilic silica. This experimental result confirms our finding from TEM pictures that the final dispersion state of silica and morphology of the blend do not depend on the preparation procedure. Vermant et al. [24] came to the same conclusion for PIB/PDMS 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. However, fitting the Palierne model to filled blend could have turned out to be difficult. How to take into account the silica contribution to the viscoelastic behaviour of the blend as the silica fillers are expected to significantly influence both interfacial tension and viscosity ratio? Few years ago, we used the Palierne model [36,37] in the case of crystallisation 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, Einstein law cannot be applied due to the fractal structure of these particles even at low concentration. Consequently, the Palierne model was applied using the experimental viscoelastic data of filled PP (or PS) samples. 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

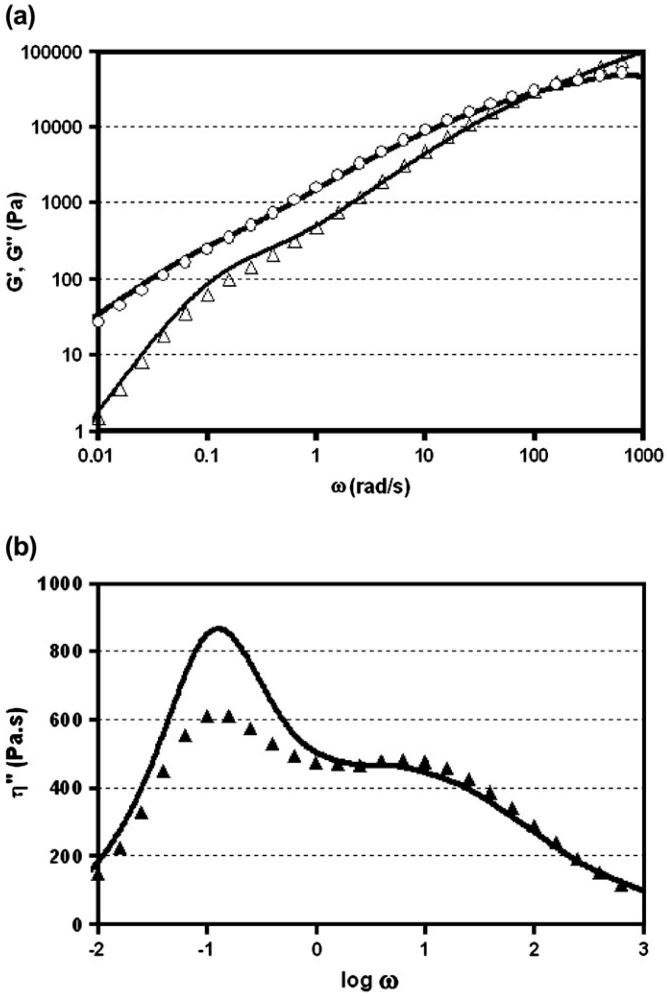

Fig. 8. Modelling of the viscoelastic behaviour of PP/PS 70/30 blend from Palierne model, $T = 200\,°C$. (a) Frequency dependence of the complex shear moduli and (b) frequency dependence of $\eta''(\omega)$.

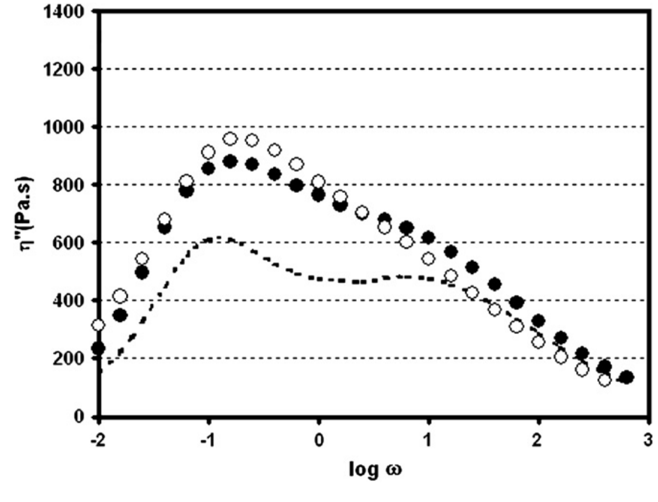

Fig. 9. Frequency dependence of η'' for PP/PS blend filled with 3% silica particles. The silica particles have been simultaneously dispersed in PP/PS blend during mixing. (●) Hydrophobic silica (R805), (○) hydrophilic silica (A200), and dotted line: experimental virgin blend.

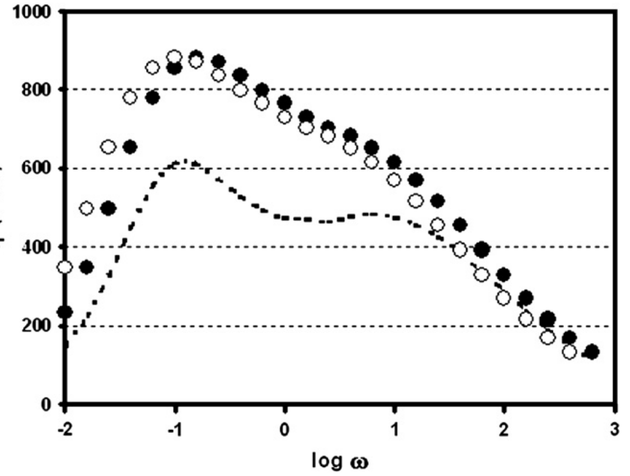

Fig. 10. Frequency dependence of η'' for PP/PS 70/30 blend filled with 3 wt% of A200 hydrophilic silica (●) silica particles dispersed in PP/PS blend during blend mixing (procedure 1), (○) silica particles pre-dispersed in PP phase (procedure 2).

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 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 4.2 and 0 wt%, respectively.

Actually, these situations can be only investigated from a pure conceptual point of view as we cannot access precisely to the silica concentration in each phases due to its partition. Also, the quality of the silica dispersion with silica particles well individualized or more or less agglomerated plays an important role on the rheological properties. In the present calculation we assumed that the silica dispersion state in each phase according to the three previous hypotheses is the same as the silica dispersion in pure phase. Consequently, we used the viscosity data presented in Fig. 3a and b.

An interesting objective would be to elucidate the mechanisms of the stabilization of the blend morphology with the help of the rheological modelling. Indeed, a very important point is that the silica plays 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 γ_{12}/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 R805 silica.

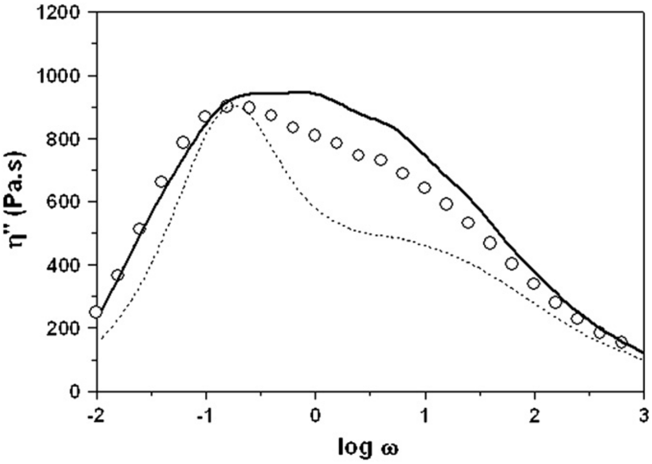

Fig. 11. Frequency dependence of η'' for PP/PS 70/30 blend filled with 3 wt% of A200 hydrophilic silica. (○) experimental data. Modelling from the Palierne model assuming: full line: if the silica is confined in PS phase (10 wt%) and dashed line: if the silica is homogeneously dispersed (3 wt%).

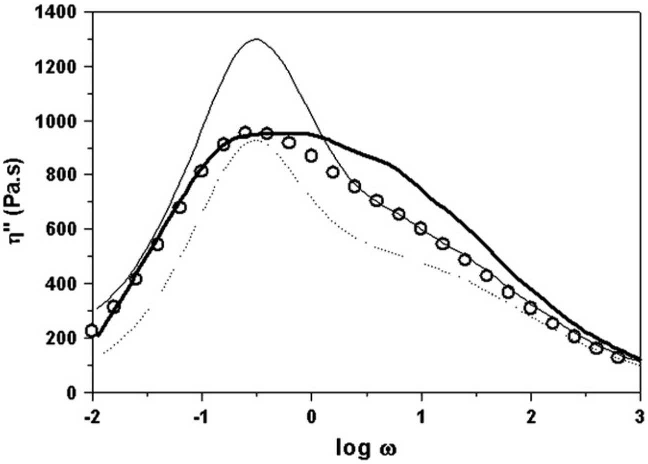

Fig. 12. Frequency dependence of η'' for PP/PS 70/30 blend filled with 3 wt% of R805 hydrophobic silica. Modelling from the Palierne model assuming: thick full line: if the silica is confined in PS phase (10 wt%), thin full line: if the silica is confined in PP phase (4.2 wt%), and dashed line: if the silica is homogeneously dispersed (3 wt%).

Figs. 11 and 12 show the modelling from the Palierne model of the frequency dependence of η'' for PP/PS blends filled with hydrophilic (A200) and hydrophobic (R805) silica, respectively. As previously discussed, three situations have been investigated for the development of the Palierne model in the present study. The dashed line is derived from the assumption that the silica particles have totally migrated to the PS phase whereas the solid line is derived from the assumption that silica particles are homogeneously dispersed in the two phases. Regarding blends filled with hydrophobic silica, the thin full line is derived from the assumption that the silica is localized mainly in PP matrix (4.2 wt%). The values of γ_{12}/R_v and γ_{12} are reported in Table 2. From these values, it can be observed that the interfacial tension calculated from the Palierne model depends strongly on the assumptions made on the silica partition. In other words, the fitting procedure for the interfacial calculation depends strongly on the viscosity ratio of the two phases. As previously explained, this viscosity ratio is extremely difficult to calculate precisely due to the fractal nature of the silica, the fact that its state of agglomeration is not known precisely, and also because of its partition in both polymer phases. However, the TEM observations and the best fit (dotted line, Fig. 11) of the Palierne model, converge to assert that the silica particles are confined in PS phase in the case of the hydrophilic silica only. Our results show that hydrophilic silica tends to decrease the apparent interfacial tension from 2.15 to approximately 0.085 mN/m. Such behaviour was already demonstrated by Hong et al. [17] who reported, from extensional force measurements, an interfacial tension reduction in PBT/PE/clay nanocomposite varying from 57.6 to 1.4 mN/m. In the case of hydrophobic silica, the situation is quite difficult to investigate from the Palierne model as the particles form an interphase layer. First we know that the situation where the silica is confined in PS is unrealistic and thus, the calculated decrease of the interfacial tension cannot be the cause for the stabilization. On the other hand, cases 1 and 3 describe qualitatively the rheological properties and better correspond to the actual distribution of the silica. According to these hypotheses on the viscosity ratio, the Palierne model shows that the interfacial tension does not decrease with the presence of hydrophobic silica and consequently cannot explain the smaller diameter of the PS domains. We conclude that the existence of the hydrophobic silica layer interphase (that was not taken into account in the model) explains the stabilization of the blend morphology, the ‘‘shell’’ of rigid particles preventing the coalescence of PS droplets. This assumption agrees with the work of Vignati and Piazza [10] and Vermant et al. [24] who argued that leaving steric hindrance or surface rheology effect is the most probable mechanism of morphology stabilization.

4. Conclusion

The effect of two types of fumed silica (hydrophilic and hydrophobic) on the morphology of PP/PS 70/30 blends was investigated.

- First of all, a significant reduction in the PS droplets size was observed in the presence of both types of silica. Typically, the volume droplet radius decreases from 3.25 to nearly 1 μm for filled blends with 3 wt% silica. The hydrophilic silica was found to be slightly more effective.
- SEM and TEM image analysis proved that the hydrophilic silica tends to confine in the PS phase whereas hydrophobic one was located at the PP/PS interface and in the PP phase. For the latter case, images show that the interface between PP and PS has been changed by an interphase PP/silica/PS of a hundred of nanometers thick. These observations agree well with the predictions derived from the estimations of the surface tensions of the components of the blend.
- With the blending procedure consisting in pre-blending silica particles in PP matrix, a migration of hydrophilic silica from PP phase toward PS 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 particle in the two phases and its influence on viscosity ratio, limited 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. A third case of silica dispersion has been investigated compared with hydrophilic one. 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 can then concluded that stabilization mechanism of PP/PS blend by hydrophilic silica is the reduction in the interfacial tension whereas hydrophobic silica acts as a rigid layer preventing the coalescence of PS droplets.
- Apart from the role of silica in blend morphology development, we showed that hydrophilic silica can considerably change the thermo-oxidative stability of PP phase (degradation by scission of the chains). This phenomenon, which is of importance for academic investigations and industrial applications, is probably due to interaction between silica surface and thermal stabilizers.

Acknowledgments

The authors wish to thank P. Alcouffe and G. Martin for their previous help with the TEM experiments. One of the authors, L.E is very grateful for the financial grant provided by the Syrian Government.

References

[1] Ramsden W. Proc R Soc London Ser A Math Phys Eng Sci 1903;72: 156–64.
[2] Pickering SU. J Chem Soc Trans 1907;91:2001–21.
[3] Tambe DE, Sharma MM. Adv Colloid Interface Sci 1994;52:1–65.
[4] Binks BP, Lumsdon SO. Langmuir 2000;16:2539–47.
[5] Binks BP, Kirkland M. Phys Chem Chem Phys 2002;4:3727–33.
[6] Binks BP, Whitby CP. Langmuir 2004;20:1130–7.
[7] Aveyard R, Binks BP, Clint JH. Adv Colloid Interface Sci 2003;100: 503–46.
[8] Binks BP, Whitby CP. Colloids Surf A Physicochem Eng Aspects 2005;253:105–15.
[9] Binks BP, Philip J, Rodrigues JA. Langmuir 2005;21:3296–302.
[10] Vignati E, Piazza R. Langmuir 2003;19:6650–6.
[11] Ray SS, Pouliot S, Bousmina M, Utracki LA. Polymer 2004;45:8403–13.
[12] Ray SS, Bousmina M. Macromol Rapid Commun 2005;26:1639–46.
[13] Austin JR, Kontopolou M. Polym Eng Sci 2006;46(11):1491–501.
[14] Wahit MU, Hassan A, Rahmat AR, Lim JW, Mohd Ishak ZA. J Reinf Plast Compos 2006;25(9):933–55.
[15] Si M, Araki T, Ade H, Kilcoyne ALD, Fisher R, Sokolov JC, et al. Macromolecules 2006;39(14):4793–801.
[16] Hong JS, Namkung H, Ahn KH, Lee SJ, Kim C. Polymer 2006; 47(11):3967–75.
[17] Hong JS, Kim YK, Ahn KH, Lee SJ, Kim C. Rheol Acta 2007;46:469–78.

[18] Maiti S, De S, Bhowmick AK. Rubber Chem Technol 1992;65(2):293–302.

[19] Gubbels F, Jerome R, Vanlathen E, Deltour R, Blacher S, Brouers F. Chem Mater 1998;10:1227–35.

[20] Clarke J, Clarke B, Freakley PK, Sutherland I. Plast Rubber Compos 2001;30:39–44.

[21] Hrnjak-Murgic Z, Jelcic Z, Kovacevic V, Mlimac-Misak M, Jelencic J. Macromol Mater Eng 2002;287:684–92.

[22] Zhang Q, Yang H, Fu Q. Polymer 2004;45:1913–22.

[23] Thareja P, Velankar S. Rheol Acta 2007;46:405–12.

[24] Vermant J, Cioccolo G, Golapan Nair K, Moldenaers P. Rheol Acta 2004;43:529–38.

[25] Palierne JF. Rheol Acta 1991;29:204–14.

[26] Saltikov SA. Stereology. In: Elias H, editor. Proceedings of second international congress for stereology. New York: Springer-Verlag; 1967. p. 163–73.

[27] Cassagnau P. Polymer 2003;44(8):2455–62.

[28] Inoubli R, Dagréou S, Lapp A, Billon L, Peyrelasse J. Langmuir 2006;22:6683–9.

[29] Owens Daniel K, Wendt RC. J Appl Polym Sci 1969;13(8):1741–7.

[30] Guggenheim EA. J Chem Phys 1945;13:253–61.

[31] Riemann RE, Cantow HJ, Friedrich C. Macromolecules 1997;30:5476–84.

[32] Huo Y, Groeninckx G, Moldenaers P. Rheol Acta 2007;46(4):507–20.

[33] Deyrail Y, Fulchiron R, Cassagnau P. Polymer 2002;43:3311–21.

[34] Funke Z, Schwinger C, Adhikari R, Kressler J. Macromol Mater Eng 2001;286:744–51.

[35] Palmer G, Demarquette NR. Polymer 2003;44:3045–52.

[36] Cassagnau P, Espinasse I, Michel A. J Appl Polym Sci 1995;58(8):1393–9.

[37] Pesneau I, Cassagnau P, Fulchiron R, Michel A. J Polym Sci Part B Polym Phys 1998;36(14):2573–85.