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How nucleating particles migration affects the fractionated crystallization of isotactic polypropylene/polystyrene immiscible blends

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A B S T R A C T

We investigate the inter-phase migration of nucleating particles and their effect on the fractionated crystallization of polypropylene droplets dispersed in an immiscible polystyrene matrix by preparing melt-mixed 90/10 wt% PS/PP blends with selected nucleating agents. Different concentrations of nucleating agents (NAs): Phtalocianene Blue, NA11, Talc, and sodium benzoate, were initially incorporated either in neat PP or in neat PS. Then the different PS/PP/NAs blends were prepared. Contact angles were determined for the neat polymers and the NAs, and the results indicated that, from a thermodynamics point of view, all NAs should remain or migrate to the PS phase. According to SEM observations, a sea-island morphology was obtained that did not vary with NA addition. Hence the results should be independent of differences in the morphology.

PP droplets crystallized in neat blends in three well-differentiated crystallization peaks (i.e., fractionated crystallization). The NAs induce a concentration-dependent increase in the high-temperature crystallization peak at the expense of reducing the low-temperature peaks, as droplets become in contact with or contain the NAs. When compared at a constant concentration in one of the phases, the nucleating agents have efficiencies that decrease in the order: Pht Blue ≈NA11>Talc>Sod Benz. Surprisingly, for the three most effective NAs, it was found that adding them initially to the PS phase led to a much higher nucleation efficiency (evaluated in terms of increases in peak crystallization temperature) than adding them to PP. This indicates that these NAs, initially present in the PS phase, migrate to the interface or to the bulk of the PP phase (against thermodynamics). Sod Benz was the only exception, as it shows a higher thermodynamic affinity to the PS phase. We explain the migration of most particles from the PS phase to the phases' boundary or to the bulk of the PP droplets by considering that kinetic factors dominate the behavior, as, from a rheological perspective, the minor component (PP) always displays a lower viscosity than the matrix component (PS) under the chosen mixing conditions.

1. Introduction

Polymer nucleation often initiates at the interface with impurities or heterogeneities present in the bulk sample, which act as primary heterogeneous nuclei. The primary nucleation step can be largely affected if the semicrystalline polymer is mixed with a second immiscible polymer.

In particular, the phenomenon of fractionated crystallization might be found when the semicrystalline component is the minor phase in an immiscible blend [1–3]. In fact, the number of the microdomains of the dispersed phase can be of the same order of magnitude or exceed that of the nucleating impurities. In such a case, some of the microdomains (commonly polymer droplets) will be free of any heterogeneity. A typical DSC cooling trace of this immiscible blend will display several crystallization exotherms attributed, in order of increasing undercooling, to very active nucleating heterogeneities, less efficient impurities, nucleation at the interface with the matrix, and homogeneous nucleation.

During the mixing process of two immiscible polymers, the

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nucleating heterogeneities of the droplets (minor phase) could be transferred to the matrix phase. The opposite situation, i.e., migration of heterogeneities from the matrix to the dispersed phase, is also possible, in principle.

Bartczak et al. have investigated in detail the possibility of impurity transfer during melt blending of isotactic polypropylene (PP) with several different components, namely high-density polyethylene (HDPE) [4], low-density polyethylene (LDPE) [5], ethylene-propylene random copolymer (EP) [6] and atactic polystyrene (PS) [7]. The nucleation density of PP was measured by quantifying the overall crystallization rate via DSC or by polarized optical microscopy. It was found that the number of PP nuclei per unit volume either decreases [4,5] or increases, [6,7] depending on the specific blend system, increasing the amount of the second component in the blend and the mixing time. This result clearly indicates a transfer of nucleating heterogeneities between the two polymers. The concept was tested by purposely adding nucleating agents to either of the polymers. It was shown that an equilibrium PP nucleation density is achieved after sufficient mixing time, independently from the polymer that was hosting the nucleating agents at the beginning of the blending stage. It was then concluded that the driving force for the migration is of thermodynamic origin and can be quantified by the difference between the interfacial free energies of the impurities with respect to both blend components.

The topic of migration of (nano)particles in immiscible polymer blends has been intensively explored more recently, with the main aim of localizing the nanofiller at the interface between components to obtain compatibilization and improved properties [8–10]. Examples of the studied particles include carbon black [11], nanosilica [12–14], carbon nanotubes [15,16] and nanoclays [17,18].

At the equilibrium, the localization of the particle is dictated by thermodynamics. The possibly uneven distribution of particles among the blended polymers can be predicted knowing the surface tensions of the three components, according to the wetting parameter, ω_{12}:

$$\omega_{12} = \frac{\gamma_{P-2} - \gamma_{P-1}}{\gamma_{1-2}} \tag{1}$$

where $\gamma_{P\text{-}i}$ is the interfacial tension between the particle and the polymer i, and γ_{1-2} is the interfacial tension between the two polymers. When $\omega_{12} > 1$the particle is located only in polymer 1, for values of $\omega_{12} < -1$ the particle is exclusively found in polymer 2, while for other values, the particle concentrates at the interface between the two polymers. It must be underlined that particle migration cannot be achieved under static conditions, but it only occurs under the action of shear forces as a result of particle-polymer droplets collisions [8,13].

Besides the above-mentioned equilibrium considerations, it should be reminded that mixing is a dynamic process, and several kinetics effects can arise and dominate over the thermodynamics, depending, for instance, on the mixing procedure (whether the particle is first mixed with the most or least favourable phase), the viscosity ratio and mixing time [8]. For example, carbon nanotubes, which, accordingly to wettability, should be selectively located in the polylactide (PLA) phase of a polylactide/polycaprolactone (PCL) blend, are found in the PCL phase because of its lower viscosity [16]. Similar findings are reported for carbon black particles in different blends [19,20]. By tuning the mixing time, Gubbels et al. could confine carbon black particles in a HDPE/PS blend in either of the polymers or at the interface between them [21].

In the present work, we want to investigate the effect of migration of purposely added nucleating particles on the fractionated crystallization of the dispersed PP droplet phase in PS/PP blends. We have recently shown that heterogeneous particles can efficiently nucleate PP droplets [22,23]. In the previous works, the different additives were mixed directly with the semicrystalline phase, before final blending with the immiscible matrix. In this study, instead, we aim to check the possibility of impurity transfer between the two components. Several nucleating particles, chosen by their different affinity for the two blend components, are selected. The role of additive concentration in both phases on the fractionated crystallization of the droplet ensembles is evaluated via differential scanning calorimetry.

2. Materials and methods

An isotactic polypropylene, provided by Borealis Polyolefine GmbH (Austria), with weight-average molecular weight (M_W) and polydispersity index (M_w/M_n) of 365 kg/mol and 5.4, respectively, was employed as the crystallizing minor blend component. An atactic polystyrene from Sigma-Aldrich with M_W and M_W/M_n of 350 kg/mol and 2.1, respectively, was used as the matrix polymer.

Four different known nucleating agents (NAs) for PP were used in this study. Phthalocyanine blue pigment (Pht Blue), (sodium 2,2′-methylene bis-(4,6-di-tert-butylphenyl) phosphate) (NA11), and talc were kindly provided by Borealis Polyolefine GmbH, in the form of fine powders. Sodium benzoate (Sod Benz) was purchased from Sigma-Aldrich. All the materials were used as received.

All the blends were prepared in a Brabender Plastograph W 50 internal mixer at 200 °C, using a rotor speed of 100 rpm for 10 min. The mixing strategy was the following: masterbatches of the two polymers containing different concentrations of the various nucleating agents were first prepared, then each of the nucleated polymers were mixed with the neat second component at a constant weight concentration (90 wt% PS and 10 wt% PP). A blend with neat PS and PP was also prepared for comparison under the same mixing conditions. Table 1 reports all the prepared compositions, in which the weight concentration of the polymers in the additivated samples represents the content of polymer masterbatches. For the sake of shortening the blends nomenclature, since all blends have the 90/10 composition, the 90/10 code will not be reported in the following.

The additive concentrations were chosen according to the capabilities for accurate weighting. The blends in which the NAs were added to PP covers the lower range of overall additive concentration in the

Table 1
Composition of the prepared blends expressed in wt%. NA refers to each of the employed nucleating agents (i.e., Pht Blue, NA11, Sod Benz, or Talc), whereas the asterisk (*) refers to the polymer in which the nucleating agent is added.

Samples	PS (wt %)	PP (wt %)	NAs in PP (wt %)	NAs in PP (wt %)	Overall conc. of the NA in the blend (wt %)
90/10 PS/PP			0	0	0
90/10 PS/PP* (+0.25 NA)	90	10	0.25		0.025
90/10 PS/PP* (+0.5 NA)	90	10	0.5		0.05
90/10 PS/PP* (+0.75 NA)	90	10	0.75		0.075
90/10 PS/PP* (+1 NA)	90	10	1		0.1
90/10 PS/PP* (+3 NA)	90	10	3		0.3
90/10 PS* (+0.07 NA)/PP	90	10		0.07	0.063
90/10 PS* (+0.15 NA)/PP	90	10		0.15	0.135
90/10 PS* (+0.25 NA)/PP	90	10		0.25	0.225
90/10 PS* (+0.5 NA)/ PP	90	10		0.5	0.45
90/10 PS* (+0.75 NA)/PP	90	10		0.75	0.675
90/10 PS*(+1 NA)/PP	90	10		1	0.9

blends, while those where the NAs were added in PS attain a maximum concentration of about 1 wt%. A partial overlap exists between the two series, in the range of overall concentrations 0.06–0.3 wt%.

Scanning Electron Microscopy (SEM) analysis of the internal surfaces of the blends was performed. At first, the samples were cryo-fractured under liquid Nitrogen, and then they were sputter-coated with thin carbon layers (Polaron E5100). The morphology of the different NAs was also observed via SEM. A field emission instrument (Supra 40 VP model, Zeiss, Germany) was used.

The crystallization kinetics of the various blends was investigated via differential scanning calorimetry (DSC). Samples of about 3–5 mg were inserted in aluminum pans and analyzed with a DSC1 STARe System (Mettler-Toledo, Switzerland), under a constant nitrogen flow of 20 mL/min. The DSC was calibrated with indium. All the samples were first heated to 210 ºC, kept there for 3 min to erase any previous thermo-mechanical treatment, then cooled to − 10 ºC and subsequently heated again to 210 ºC with scan rates of 10 K/min.

The surface tension of the different components was determined by measuring the contact angles with two probe liquids (water and diiodomethane) with a contact angle meter One Attension Theta. PP and PS thin films were prepared for the determination of the contact angle by manual compression molding on a hot plate. Contact angles of solid powder substrates with a test liquid is an established method to obtain the wettability of particles [24,25]. For measurements of the various NA particles, tablets were prepared by compressing a small amount of powder in a Specac Vertex 70 press, under a pressure of 10 ton for a few minutes.

Rheological analysis was performed using an HR 10 rheometer (TA Instruments, USA). The polymers were prepared in the form of approximately 1 mm-thick plates with a compression molding press and subsequently subjected to a frequency sweep test at 200 °C, consistent with the adopted blending temperature. Specifically, the rheological measurements were carried out in a range of frequencies from 0.01 to 100 rad/s, using an oscillation amplitude of 3% (within the linear viscoelastic range).

3. Results and discussion

The surface tensions of the various solid substrates, polymers, and NAs were determined by measuring the contact angles with two test liquids, water, and diiodomethane. The average values of the contact angles are reported in the Supporting Information, Table S1. From these values, the interfacial free energy of the solid substrate can be evaluated according to: [26]

$$\frac{\gamma_l(1+\cos\theta)}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^d} + \sqrt{\gamma_s^p}\left(\frac{\sqrt{\gamma_l^p}}{\sqrt{\gamma_l^d}}\right) \tag{2}$$

where γ_l is the surface tension of the liquid, θ is the contact angle, γ_s is the surface tension of the solid substrate, and the superscripts d and p are related to the dispersive and polar component of the interfacial free energies, respectively. By using two probe liquids, a set of two equations can be written, from which the values of the two unknown variables (γ_s^d, γ_s^p) are found.

The values of the interfacial free energies for the various solids are reported in Table 2. The values found for PP and PS are in excellent and good agreement with the literature, respectively. [12] The solid additives have larger surface energies, which increase in the order: Pht Blue <NA11<Talc<Sod Benz.

Once the polar and dispersive components of the surface tensions are known for all the blend constituents, the polymer/polymer and particle/polymer interfacial tensions can be calculated with the use of the Owens-Wendt equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d\gamma_2^d} - 2\sqrt{\gamma_1^p\gamma_2^p} \tag{3}$$

where the subscripts *1* and *2* refer to the considered constituents (e.g., particle/polymer or polymer 1/polymer 2).

From the values of the interfacial tensions of the different blend components, the wettability parameter of the various NAs can be evaluated using equation 1. Table 3 shows the interfacial tensions of the different particles with the two polymers. The wettability parameters of the same particles are calculated using equation 1, with polymer 2 being PS and polymer 1 being PP.

The obtained values demonstrate that for all the particles, the surface tensions with respect to PS are lower than those with respect to PP. This suggests that migration of the particles towards the PS matrix during blending will be favoured. In fact, all the wettability parameters are clearly lower than −1, indicating the preferential location of the NAs in the PS phase, from the thermodynamics standpoint. In particular, the affinity for the polystyrene matrix is maximum for Sod Benz and minimum for Pht Blue, with intermediate values found for Talc and NA11 (Talc<NA11). It should be noted that the wettability parameters are calculated at room temperature since the temperature coefficient of the surface tensions of the various additives is unknown. As such, they might differ from the actual ones which are established at the mixing temperature of 200 °C. Therefore, the obtained values should be considered only as an approximation of the real ones, notwithstanding they are useful for further data interpretation and discussion.

After the initial thermodynamic characterization of the systems, the morphological aspects of the prepared blends are considered. Selected SEM micrographs of additivated blends are compared in Fig. 1. Samples containing 1 wt% of NAs added either in PP or in PS are chosen for comparison, together with the neat PS/PP blend. As expected, all blends exhibit the typical droplet-in-matrix morphology, which is characteristic of a 90/10 PS/PP composition [2,22,23]. No apparent differences in the PP droplet size are found when the NA is added, either in the dispersed or in the matrix phase, for all the investigated particles. Moreover, the droplet diameter also seems unaffected by the type of added particle.

The PP droplet size distribution was quantitatively determined by an image analysis software. The results for the selected concentration of NAs, added either in PP or PS, are shown in Figs. 2a and 2b, respectively. The bar plots highlight the following facts: i) the type of particle does not affect the obtained average droplet size; ii) increasing the concentration of the NAs does not meaningfully vary the PP droplet size; iii) mixing the additive in PP or PS does not significantly change the droplet size; iv) considering the relative standard deviation of the droplet size distribution, the blends containing the additives are comparable to the neat blends. It can thus be concluded that the addition of NAs practically does not influence the morphology of the blends. Therefore, the crystallization data presented in this contribution can be safely considered to be the result of the sole effect of NA incorporation and their possible

Table 2
Surface tensions of the employed polymers and nucleating agents.

Materials	γ [mN/m]	γ^p [mN/m]	γ^d [mN/m]
PP	30.9	0.0	30.9
PS	36.6	1.4	35.2
Pht Blue	46.2	6.8	39.4
NA11	50.4	27.5	22.9
Talc	54.2	16.7	37.5
SodBen	71.5	44.0	27.5

Table 3
Values of the interfacial free energies (with respect to PP and PS) and of the wettability parameters of the used nucleating agents.

Materials	γ^{PP} [mN/m]	γ^{PS} [mN/m]	ω_{12}
Pht Blue	6.6	2.1	−3.6
Talc	15.9	8.4	−6.0
NA11	26.7	17.8	−7.1
SodBen	42.3	30.1	−9.7

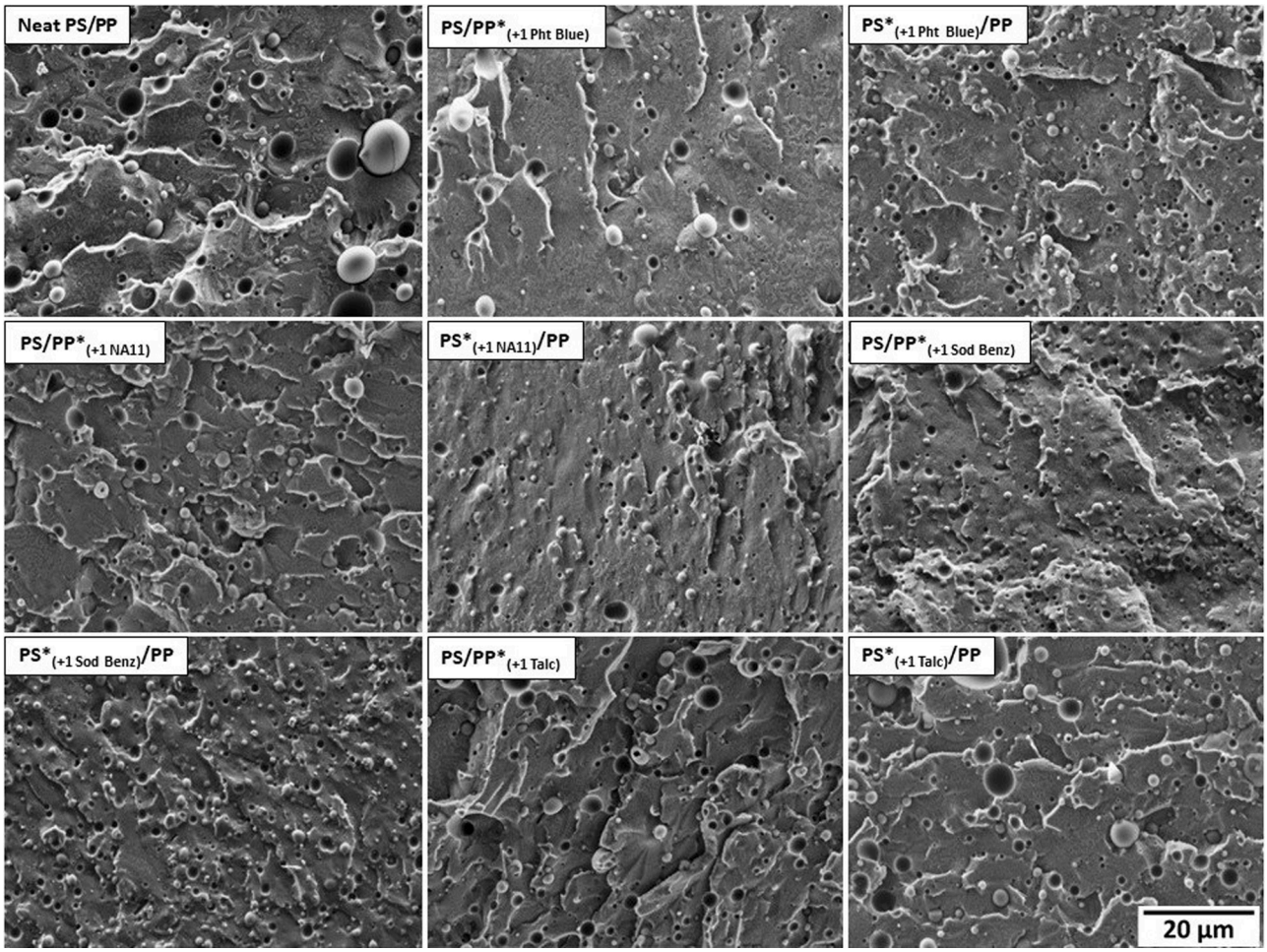

Fig. 1. SEM micrographs of the neat blends and blends with 1 wt% of the NAs added either in the PP or in the PS phase.

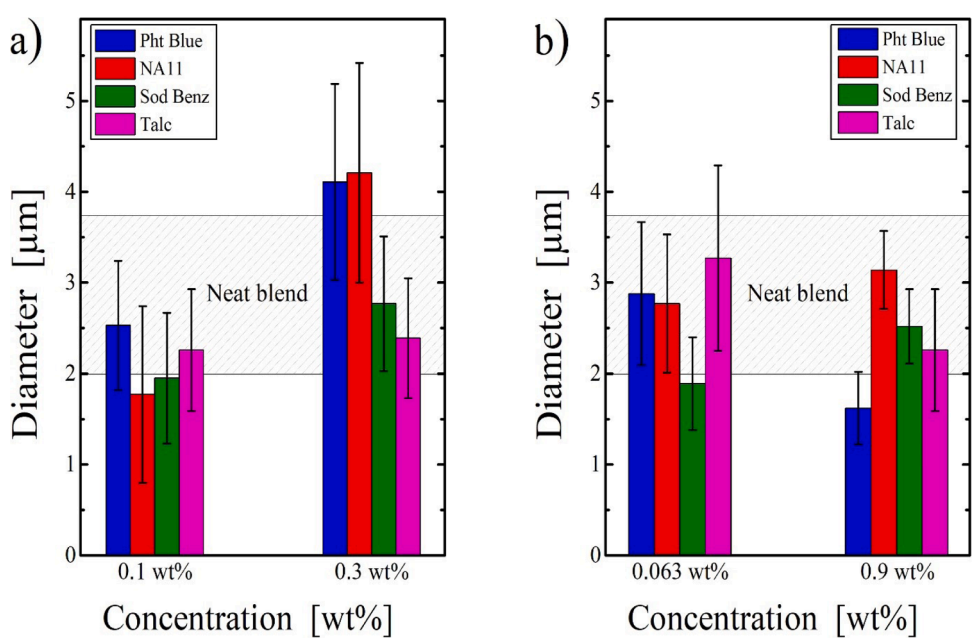

Fig. 2. Average sizes (and related standard deviations) of the PP microdomains in the 90/10 PS/PP blends at the indicated overall concentrations of additive: (a) corresponds to blends where NAs are mixed with PP first, whereas (b) refers to blends where NAs are added to the PS phase before mixing with PP. The shaded area represents the size interval (standard deviation around the average value) of the PP droplets in the neat PS/PP blend.

migration among the two phases.

In addition to that of the blends, the morphology of the nucleating particles has been checked as well. Representative SEM images and average sizes of the various NAs are reported in Fig. S1 and Table S2 of the Supporting Information, respectively. Although some of the particles exhibit larger sizes with respect to PP droplets, we note that the actual morphology after blending could be largely different due to possible particle fracture under the action of shear forces.

Next, the non-isothermal crystallization results of the different nucleated blends are considered. Fig. 3 reports the effect of increasing NA concentration either in PP (a,c) or PS (b,d) phase for two nucleating additives, namely NA11 (a,b) and Sod Benz (c,d). At first, the crystallization of the neat PS/PP blend is analysed. A typical fractionated crystallization behavior can be observed, with at least three distinct

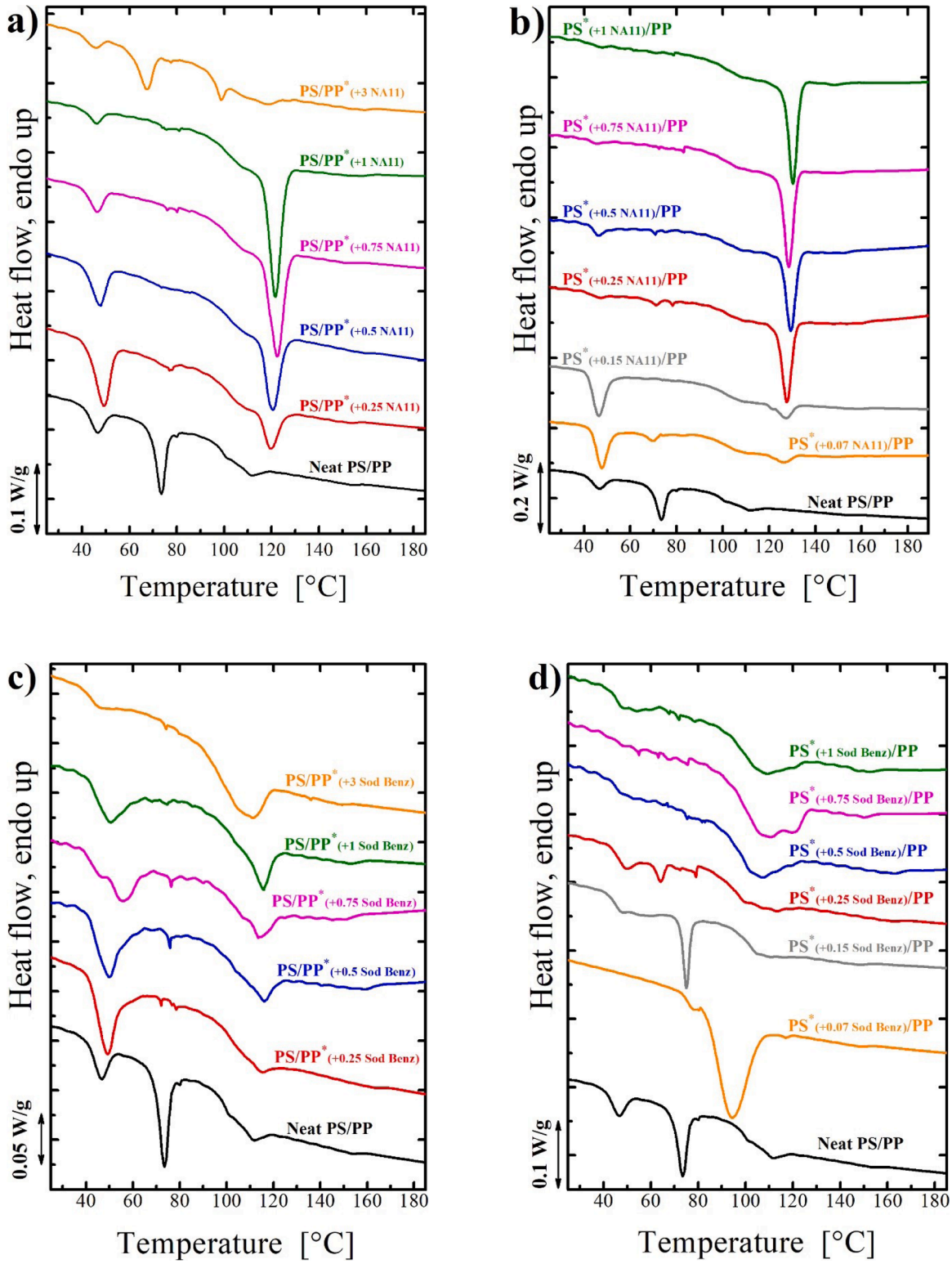

Fig. 3. DSC curves during cooling from the melt for 90/10 PS/PP blends additivated with NA11(a,b) and Sod Benz (c,d) at different concentration either in the PP (a, c) or PS (b,d) phases.

exothermic peaks located at about 110, 75 and 45 °C. These events can be related, from high to low temperatures, to naturally occurring nucleating impurities in PP, PS interface, and homogeneous nucleation of the droplet population with smallest sizes, respectively [2,22,27]. This is consistent with the low concentration of PP in the blend and the small average droplet size with a relatively wide dispersion.

Considering the blends containing NA11 added to PP (Fig. 3a), it can be seen that with increasing particles concentration in the dispersed phase, a crystallization event at lower undercoolings (around 120 °C) develops and increases in intensity at the expense of the peak at 75 °C first, and more gradually of the peak at 45 °C. The high crystallization temperature peak increases its temperature slightly with increasing concentration, but its peak area increases with concentration significantly. This indicates a growing population of nucleated droplets, while the parallel decrease of the homogeneous nucleation peak (at 45 °C) suggests that also the droplets with the smallest sizes get gradually heterogeneously nucleated. Interestingly, the low undercooling peak tends to disappear for higher nucleating agent concentration. This effect might be due to agglomeration of the particles, thus decreasing their nucleating ability, or to a more efficient transfer to the thermodynamically favoured PS phase during mixing, because of the increased number of collisions with the higher particle concentration [13].

These results are consistent with those of Baer et al., who also studied droplets of PP in a PS matrix, but obtained via breakup of PP nanolayers and thus of smaller size. The droplets were nucleated with different soluble or solid heterogeneous nucleating agents [28–30]. Similarly to our case, it was seen that the low-temperature exotherm, characteristic of the homogeneous nucleation process, disappears in favor of a high-temperature one with increasing nucleant's concentration, provided that the size of the PP droplet was commensurate to the size of the added particle.

A similar situation occurs when NA11 is added to the PS matrix (see Fig. 3b). In particular, a peak at even lower undercoolings develops (around 125 °C) and grows with concentration. The almost complete disappearance of the homogeneous nucleation peak suggests an even higher nucleating efficiency in this case, compared to the addition of NA11 to the dispersed phase, possibly due to the higher overall particle concentration with this mixing procedure. Remarkably, despite the particle wettability values significantly lower than − 1, which would predict the location of the nucleating particles in the PS phase, nucleation of the PP droplet can still occur when the NA is added to the PS matrix. This result shows that a certain number of nucleating NA11 particles is either located at the polymer/polymer interface or has been transferred to the PP droplets during mixing, indicating a predominant kinetic effect against the thermodynamics considerations.

The effect of adding Sod Benz on PP droplets fractionated crystallization can be evaluated from Figs. 3c and 3d. It is possible to note that the nucleating effect of these particles is far less marked than that of NA11. This is evident because the crystallization peak at lower undercooling is found at lower temperatures and is by far less intense. Moreover, the droplet population that nucleate homogeneously is always present, also in samples with Sod Benz concentration of 1 wt% in the dispersed phase. Adding the nucleant to the PS phase does not significantly improve the nucleating efficiency, despite the higher overall concentration, the heterogeneous nucleation peak has a small intensity; it is broad and located at relatively low temperatures. To explain the behavior of Sod Benz, with respect to that of NA11, two factors can be considered. The first is the intrinsically lower nucleating efficiency of the former nucleant compared to the latter [22]. The second consideration is the higher affinity of Sod Benz to the PS phase, as demonstrated by the higher absolute value of the wettability parameter (Table 3). The thermodynamics thus implies a stronger driving force for the migration or selective localization of Sod Benz particles in the PS matrix, with respect to PP droplets. It should be mentioned that the recorded thermal behavior of the PS*(+0.07 Sod Benz)/PP blend (see Fig. 3d) is peculiar and out of the trend and the reason behind this was not further investigated.

The results related to Pht Blue and Talc are reported in Fig. S2 of the Supporting Information. Phtalocyanine blue pigment has a very efficient nucleating behavior, promoting the formation of a high temperature crystallization peak already at very low concentrations and independently of the initial distribution (PP vs. PS phase). Talc presents instead a nucleating efficiency intermediate between Sod Benz and NA11, it gives rise to fractionated crystallization peaks at high temperatures but of relatively low intensity. Both nucleants are effective when added to PP or PS phases, indicating the possible kinetic localization of some particles at the PS/PP interface or in the PP droplet phase.

To directly compare the nucleating efficiency of the different NAs particles, the DSC cooling curves of the blends containing the same concentration of nucleating particles dispersed firstly in either PP or PS are shown in Fig. 4.

By comparing the exotherms obtained after adding a constant weight percent of the different NAs in the dispersed PP phase (Fig. 4a), it can be deduced that Pht Blue is the most efficient nucleating agent, as the high temperature crystallization peak is the sharpest and with the largest area. The second in the rank is NA11, for which the heterogeneously nucleated PP droplets crystallize at a temperature comparable to that of Pht Blue, but with substantially smaller enthalpy. Also, a part of the droplet ensemble is still clean of any impurity, as judged by the area of the homogeneous nucleation peak at 45 °C. Besides the possible difference in intrinsic nucleating efficiency between the two particles, this suggests that a larger number of droplets is nucleated in the case of Pht Blue with respect to NA11, possibly due to an easier migration of the particles to the interface or to the PP phase, in agreement with the lower affinity with the PS matrix deduced by the wettability parameter (Table 3).

The enthalpy of crystallization of the heterogeneously nucleated droplet fraction for the systems containing Sod Benz and Talc is much lower than that of the other two nucleants indicating a mild or low nucleating efficiency (Fig. 4). The addition of Talc gives rise to multiple exotherms in the high-temperature region, possibly because of different droplet sizes or Talc particle specific surface. Considering the same concentration of nucleants added to the PS matrix leads to the same ranking of NAs efficiency. The high-temperature peak area is typically larger (and, correspondingly, the homogeneous nucleation peak smaller) with respect to the case of NA addition in the dispersed PP phase, due to the higher overall concentration of particles in the blend (see Table 1). Again it is evidenced how, for any of the nucleating agents, the particles are not exclusively confined to the PS phase, as the thermodynamics would prescribe, but interact with PP droplets (by migration at the interface or to the bulk), being able to enhance their crystallization kinetics.

In order to exclude possible differences between intrinsic nucleating efficiency of the various NAs when added to bulk or blended PP, Fig. S3 reports the crystallization curves of the various additivated PPs, together with that of neat PP. Crystallization temperature increases of around 15 °C, 16 °C, 4 °C, and 8.5 °C for Pht Blue, NA11, Sod Benz, and Talc, respectively, were measured independently of the nucleant concentration. The observed nucleation effects of the various NAs in neat PP are thus consistent with those reported for the sample blended with PS (Fig. 4).

To better understand the ability of particle's inter-phase migration, the crystallization of blends containing the same overall concentration of NAs, but incorporated first either in the PP or in the PS phases are compared in Figs. 5a-d.

The curves of Fig. 5 are grouped and coloured according to the overall concentration of NA in the blend. Given the chosen 90/10 PS/PP blend composition, a concentration of 0.07 wt% in PS and of 0.75 wt% in PP corresponds to an approximate total NA concentration of 0.07 wt%, an overall concentration on average of 0.12 wt% is obtained with 0.15 wt% in PS or 1 wt% in PP. Finally, a global concentration of about 0.26 wt% is given by adding 0.25 wt% NA in PS and 3 wt% in the dispersed

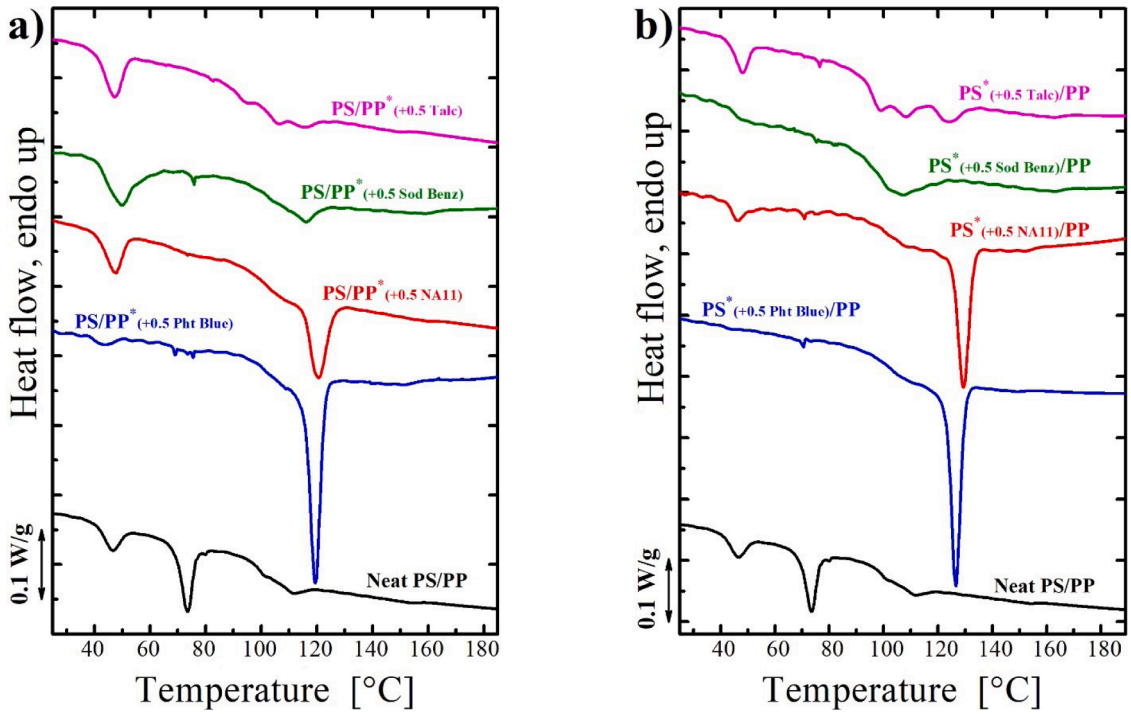

Fig. 4. DSC curves during cooling from the melt for the 90/10 PS/PP blends with 0.5 wt% of the different NAs added either in the PP (a) or PS (b) phase.

PP phase.

The data relating to phthalocyanine blue are reported in Fig. 5a. For all three overall particle concentrations, the position of the heterogeneous nucleation peak (i.e., crystallization temperature) and the enthalpy of crystallization are remarkably similar, notwithstanding the initial phase of additive incorporation. This result confirms the easiness of additive migration from PS to the PP (or to the interface), against interfacial tensions equilibrium but in agreement with the lowest possible affinity to the PS phase (i.e., lowest wettability absolute value). Interestingly the behavior is independent of nucleant concentration, evidencing that the migration can occur already at low particle loadings. NA11 particles, instead, display meaningful differences depending on the phase to which they are initially added (Fig. 5b). Considering the lowest overall concentration (0.07 wt%), when the nucleant is added to the PP dispersed phase, the heterogeneous nucleation peak around 120 °C is prominent, and the homogeneous nucleation peak is small. On the contrary, when NA11 is incorporated first in the PS matrix, the major fractionated crystallization peak is that of homogeneous nucleation at 45 °C, and the peak at low undercooling is weak. Similar behavior is found for an overall concentration of 0.12 wt%. The fact that, despite its relatively high intrinsic nucleation efficiency, NA11 does not give a meaningful contribution to PP droplet nucleation when added to the PS matrix, suggests its low tendency to migrate from PS to the interface or bulk PP phase. Or, equivalently, the NA11 has a preference to be located in the PS matrix, in agreement with the high negative value of the wettability parameter, ranking second among all the nucleants. An anomalous behavior is instead found for the highest overall concentration, where the nucleating effect when adding NA11 to PS is larger than when it is added to the PP dispersed phase. However, as previously discussed, the reason might be the too large initial concentration in the PP phase, which can cause particles agglomeration phenomena or more favourable migration of the nucleant to the PS phase.

Sod Benz nucleant (Fig. 5c) has a low intrinsic nucleating efficiency, as already discussed. Dispersing it first in PS or PP phase provokes differences in the fractionated crystallization behavior. In particular, a weak heterogeneous nucleation peak is only discernible when Sod Benz is initially added to the PP phase. The observation leads to the hypothesis that this nucleant locates preferentially in the PS matrix, which is supported by the highest thermodynamics affinity for that phase (see wettability parameters in Table 3). For what concerns Talc (Fig. 5d), the situation is similar to Sod Benz, although a small nucleating effect is also present when the particles are added initially to the PS matrix (see weak peaks above 100 °C). This might indicate that the possibility of migration between the phases exists, although it is less relevant than what was observed for Pht Blue (Fig. 5a). In fact, according to the wettability parameter, the affinity of Talc to PS is lower than that displayed by Sod Benz and NA11.

The crystallization temperatures of the heterogeneous nucleation crystallization peak (i.e., highest crystallization temperature peak) and the related enthalpies for the various blends are collected in Fig. 6 and Fig. S4, respectively. The data are represented by filled symbols when the nucleant is added first to the PP dispersed phase, or by empty symbols, for blends prepared by dispersing the particles initially in the PS matrix. As deduced from Table 1, the series of samples with nucleants in PP covers the low range of overall concentrations, while the other samples extend the range to about 1 wt%. The overlapping range of concentration spans from 0.07 to 0.26 wt%, as shown in the DSC curves of Fig. 5.

The data related to Pht Blue, NA11, and Talc (Figs. 6a, b and d) display a similar behavior: the crystallization temperature increases with the overall concentration of nucleant until an asymptotic value is reached. The highest value at saturation is reported for NA11, closely followed by Pht Blue, while Talc is about 4–6 °C lower. For the blends with nucleants initially incorporated in PS, the increase in crystallization temperature with increasing particles concentration must be related to a more efficient transfer to the droplets (or to the interface), as a result of the augmented number of particle-droplet collisions during mixing [13]. Notably, for all these NAs, the blend with the highest concentration incorporated initially in the PP phase deviates from the overall trend, showing a markedly reduced crystallization temperature. As previously suggested, the reason for this can be found in a possible aggregation of the nucleating particle, which decreases the effective surface area available for nucleation. Alternatively, an increased migration towards the thermodynamically favoured PS phase at high nucleant

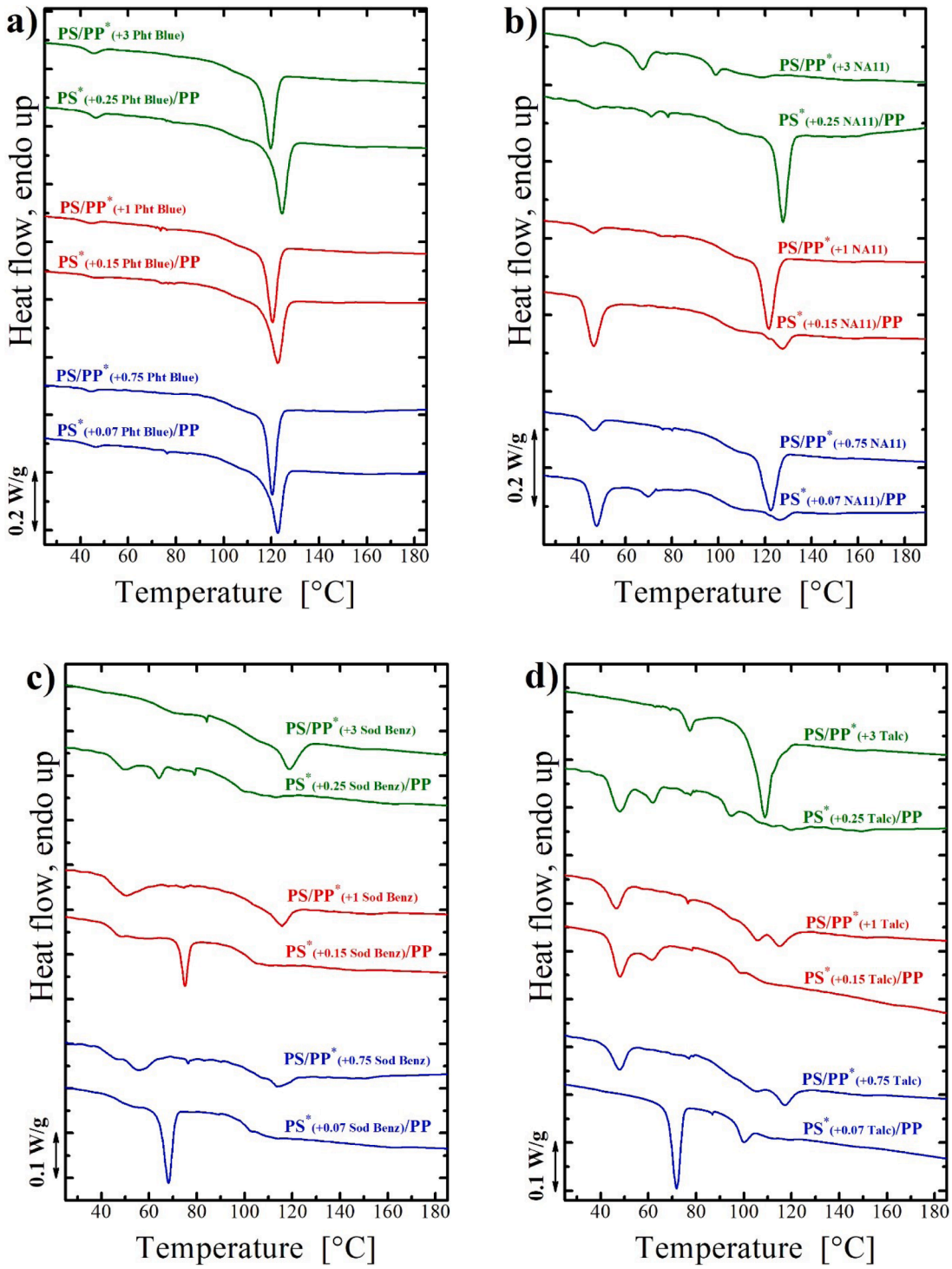

Fig. 5. DSC curves during cooling from the melt for the 90/10 PS/PP blends with a similar overall concentration of the different NAs: Pht Blue (a); NA11 (b); Sod Benz (c); Talc (d). The curves are grouped in pairs according to the overall concentration of particles in the blend, which corresponds approximately to 0.07, 0.12, and 0.26 wt%, from bottom to top.

loading is also possible. Considering the region of overlapping concentrations between the nucleants added to PP and PS, it can be seen that the crystallization temperature is always higher when the NA particles are initially incorporated in the PS matrix, rather than in the crystallizing PP phase. This result is rather counterintuitive and indicates that the effective concentration in the droplet (or at the interface between the droplet and matrix) is higher in the former case, i.e., when the NAs are firstly dispersed in the matrix. The crystallization temperature gap between the two blending strategies is particularly low for Pht Blue and Talc, while it is larger in the case of NA11. We hypothesize that this difference is correlated to the easiness of inter-phase particle migration, being substantial for Pht Blue and Talc (the NAs with the lowest affinity with the PS phase) and lower for NA11 (larger thermodynamic affinity towards the PS matrix).

A completely different situation holds for Sod Benz particles (Fig. 6c). Here the maximum crystallization temperature value achieved is the lowest among the various NAs, in agreement with its lowest intrinsic nucleation efficiency. Moreover, the increase of crystallization

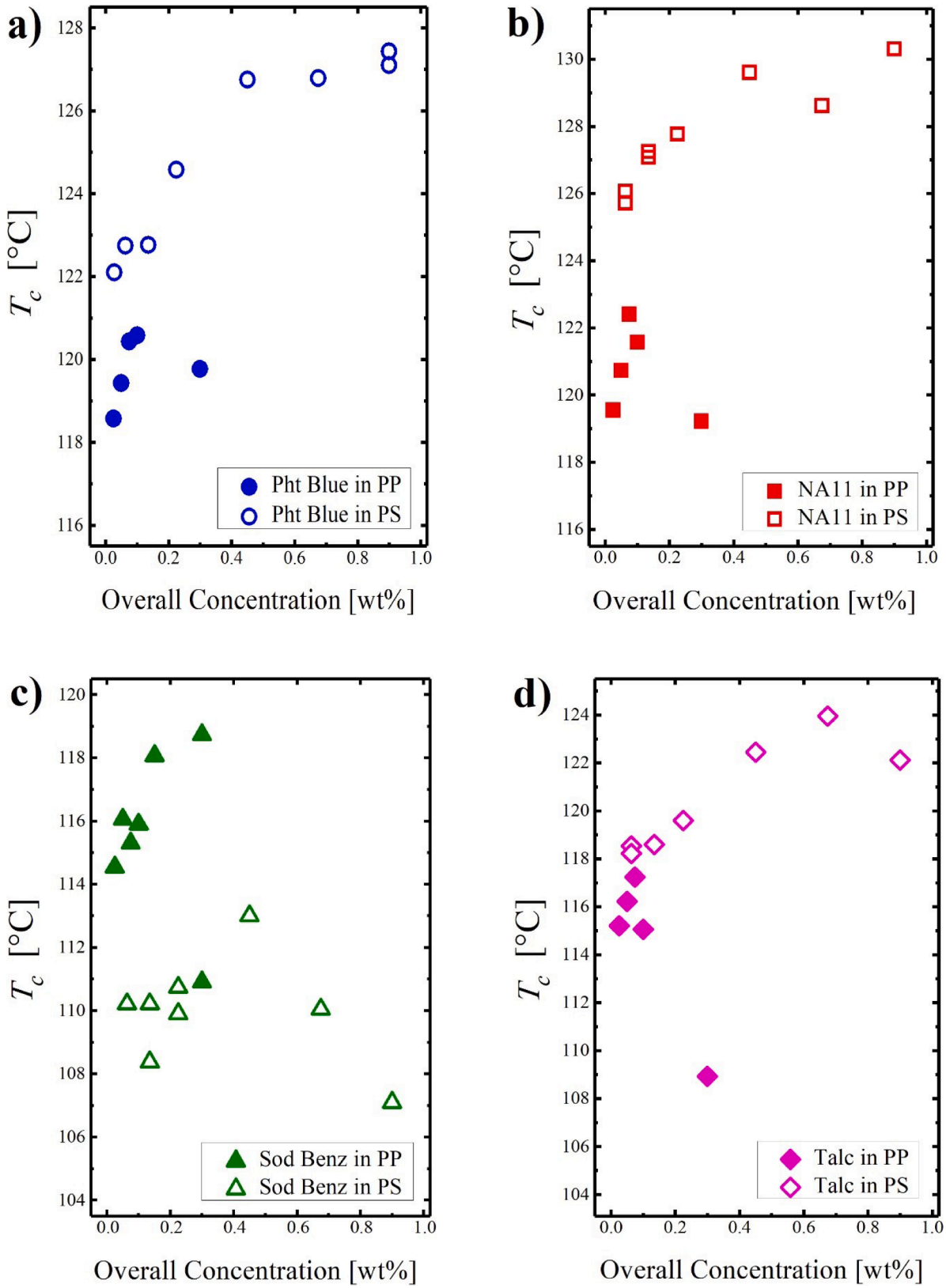

Fig. 6. Crystallization temperatures of the heterogeneous nucleation crystallization peak of the various blends, as a function of the overall NA concentration for Pht Blue(a); NA11 (b); Sod Benz (c); Talc (d). The filled symbols refer to blends where the nucleant is initially added to the PP dispersed phase, the empty ones to blends where it is first mixed with the PS matrix.

rate with increasing nucleant overall concentration is only found for samples where the particles are originally added to the PP dispersed phase (with the exception of the 3 wt% concentration, as discussed above). On the other hand, for Sod Benz added to the PS matrix at first, the trend of the data is practically flat. The most striking difference between Sod Benz and the behavior of the other NAs is, however, that for this additive the crystallization temperatures obtained when it is added to the crystallizing phase are higher than those recorded when incorporating it in PS. This is exactly contrary to the finding for Pht Blue, NA11 and Talc, reported above. It is thus deduced that, as a consequence of the higher affinity of Sod Benz for the PS matrix, when the particles are added to this latter phase, no meaningful migration to the interface or to the bulk of the PP droplets takes place, resulting in a practical absence of nucleating effect.

For what concerns the associated crystallization enthalpies, reported in Fig. S4, it can be stated that a general increasing trend is found with increasing the overall NAs concentration, indicating an increase in the number of heterogeneously nucleated droplets. The highest enthalpies are found for Pht Blue and NA11, while lower values are recorded for Sod Benz and Talc. Regarding the overlapping concentration range between the two nucleant addition strategies, it can be observed that Pht Blue presents comparable values, perhaps as a consequence of the already underlined easiness of particle migration between the phases. Instead, for the rest of the nucleants, higher enthalpies are recorded when the particles are initially located in the crystallizing PP phase, in agreement with the higher thermodynamic driving force for the localization of the particles in the PS phase, but in contrast with the larger crystallization temperatures determined for the nucleants dispersed in the PS phase (Fig. 6a,b,d). It must be deduced that when these NAs are added to the PS matrix, the nucleation is more efficient (higher crystallization temperature), but a lower number of droplets is heterogeneously nucleated (lower crystallization enthalpy).

To explore the hypothesis of correlation between the crystallization temperature gap for the same overall concentrations (with incorporation of the additive either in PP or PS) and the thermodynamic driving force for NAs migration, the average value of crystallization temperature difference (ΔT_C) is plotted against the measured wettability parameter in Fig. 7. The two overall concentrations of 0.07 and 0.12 wt% are considered only, to avoid issues with possible particle aggregation phenomena for the higher concentration (3 wt% in PP). The crystallization temperature recorded for the nucleant initially dispersed in PS has been subtracted from the one detected when the nucleant is firstly located in PP. An average ΔT_C for the two above mentioned overall concentrations is calculated.

For all the NAs, excluding Sod Benz, the ΔT_C are negative, meaning that it is more efficient from the nucleation point of view to add the nucleant's particles to the PS matrix than to the crystallizing PP phase, for the same overall NA concentration. As previously mentioned, the opposite behavior of Sod Benz must be related to its higher affinity for the PS phase, which prevents a substantial migration of the additive towards the droplet-matrix interface or to the bulk of the PP droplet phase. Interestingly, the two nucleating agents displaying the lowest affinity to the PS matrix (Pht Blue and Talc), show the lowest values of ΔT_C. This means that their migration towards PP, driven by the mechanical forces during mixing rather than by thermodynamics, is somewhat easier in these NAs. NA11, instead, presents a large temperature gap, although opposite with respect to the one of Sod Benz. This can be the result either of a certain migration from PP droplets to PS phase (assisted by thermodynamics) or of a better migration in the opposite direction (against thermodynamics), resulting in higher crystallization temperatures when the nucleant is in PS with respect to when it is in PP. The non-monotonic trend of ΔT_C as a function of the wettability parameter underlines that the migration of additives able to affect crystallization is not a sole function of thermodynamics and interfacial tensions, but other kinetic factors must come into play. These include the shear forces acting during mixing, and are thus related, for instance, to the viscosity ratio between the phases and the particle size/shape, which affects the particles' dispersion state.

To investigate these kinetics effects, and most importantly, those that lead to the remarkable migration of the particles from the PS matrix to PP droplets or the interface, opposite to the thermodynamic prescription, a rheological analysis of the two polymers under melt blending conditions was conducted. Fig. 8 reports the viscosity of PS and PP as a function of the applied shear rate at a constant temperature of 200 °C. The shear rate ($\dot{\gamma}$) representative of the mixing conditions inside the mixer chamber is indicated in the plot, and has been evaluated according to: [31]

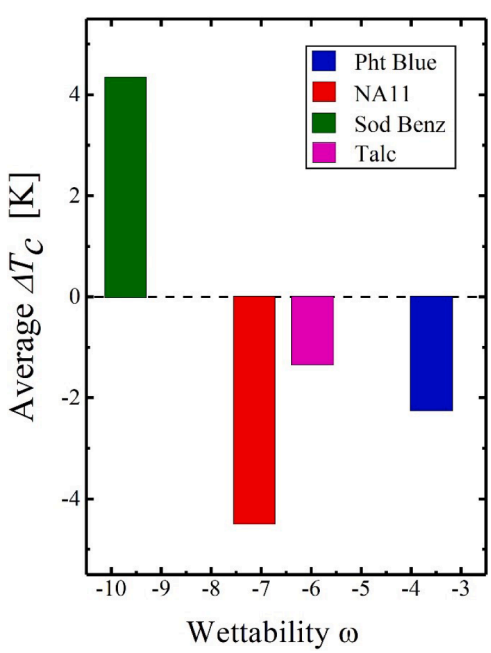

Fig. 7. Average difference in crystallization temperatures (for the overall concentrations of 0.07 and 0.12 wt%) considering the nucleant initially added to the PP dispersed phase with respect to blends where it is first mixed with the PS matrix, as a function of the wettability parameter of the various NAs.

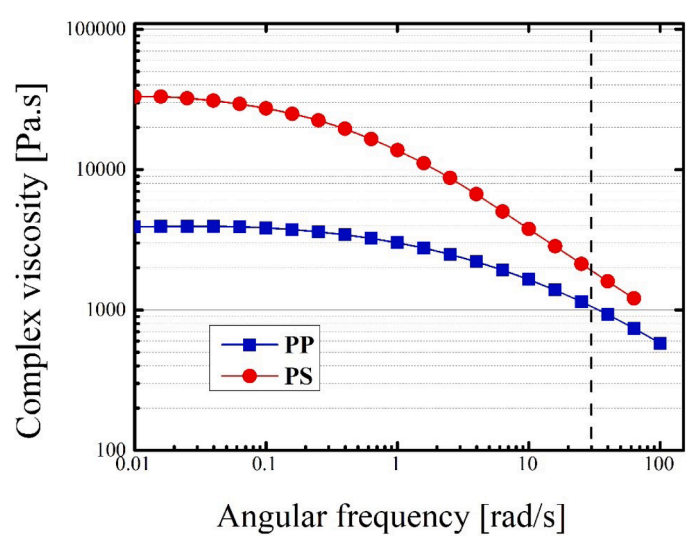

Fig. 8. Complex viscosity as a function of angular frequency for rheological measurement carried out on PS and PP at a temperature of 200 °C. The vertical dashed line indicates the average shear rate value holding during mixing in the Brabender Plastograph.

$$\dot{\gamma} = \frac{2\pi RN}{60h} \quad (4)$$

where R is the radius of the rotor blade (which changes with position), N is the rotor speed during mixing (in rpm), and h is the gap between the mixer chamber wall and the rotor blade. The average shear rate between the maximum and minimum possible values is calculated, using the following parameters, measured directly from the mixing chamber and rotors: $R_{max} = 18.5$ mm, $h_{min} = 1$ mm and $R_{min} = 10.5$ mm, $h_{max} = 9$ mm.

Notably, the viscosity of PS is always higher than that of PP, in all the investigated range of shear rates. In particular, the viscosity ratio PS/PP goes from about 8 in the Newtonian region of low shear rates to approximately 2 at the shear rate characteristic of the mixing conditions (about 30 rad/s, assuming the validity of the Cox-Merz rule [31]). As such, the PP dispersed phase is the one presenting the highest fluidity during mixing, a fact that can affect the selective localization of the NA particles. It has been shown in the literature that particle distribution among the phases opposite to those predicted by thermodynamics considerations alone could be achieved when one of the phases is characterized by a lower viscosity [16,19,20]. In fact, independently from the phase in which the particles were initially incorporated, CNT and carbon black have been shown to migrate towards the interface and into the lower viscosity phase. The results of fractionated crystallization of our systems, especially those in which the nucleants are initially incorporated in PS, are thus consistent with such migration from the thermodynamically favoured PS phase towards the interface or the bulk of the dispersed PP phase, possessing a lower viscosity.

4. Conclusions

The effect of nucleating particle migration on fractionated crystallization of polypropylene droplets in an immiscible PS matrix was investigated by adopting a dual blending strategy. Selected PP nucleating agents were initially incorporated either in the PP crystallizing phase or in the PS matrix at different concentrations.

Contact angle measurements on the polymers and particles reveal that, from the thermodynamics point of view, all the nucleating agents should be preferentially located in the PS matrix phase, because of the lower interfacial tension with this polymer with respect to PP.

The droplet-in-matrix morphology of the blend is practically unaffected by the addition of the NAs in either of the phases, thus allowing a meaningful comparison of the sole effect of NAs incorporation and interphase migration on the fractionated crystallization of PP droplets.

The fractionated crystallization behavior of PP droplets is instead largely affected by the NAs incorporation, as judged by the emergence of a crystallization peak due to heterogeneously nucleated droplets at higher temperatures, at the expense of the homogeneously and interfacially nucleated droplets crystallization at larger undercoolings. When compared at an identical concentration in one of the phases, the nucleating agents demonstrate a different efficiency, decreasing in the order Pht Blue ≈NA11>Talc>Sod Benz.

The comparison of the crystallization curves for equivalent overall concentrations, but with NAs particles dispersed first either in PP or PS, reveals similar results for Pht Blue, while for the rest of the nucleants it is more efficient (in terms of crystallization enthalpy) to initially add the nucleant to the PP phase. Despite this, it is remarkable that a meaningful nucleating effect is recorded for the nucleant original addition to the PS matrix, implying a migration of the particles to the interface or to the bulk of the PP phase (against thermodynamics).

Although the calculated wettability parameters of the various particles are of general help for understanding the observed behavior, they do not explain all the effects, as kinetic factors affecting migration probably arise during mixing. For instance, the surprising migration of most particles from the PS phase to the phases' boundary or to the bulk of the PP droplets can be tentatively explained from a rheological perspective, as the minor component displays a lower viscosity with respect to the matrix under the chosen mixing conditions.

This work provides a systematic evaluation of the effect of nucleating particle migration on crystallization in immiscible blends and can therefore help further understanding of the fractionated crystallization phenomenon.

Author statement

Seif Eddine Fenni, Mariangela Spigno, Wei Wang and Andrea Costanzo: experiments, data analysis. **Seif Eddine Fenni**: writing first draft. **Alejandro J. Müller and Dario Cavallo**: Experimental design and draft manuscript revision. **Dario Cavallo**: conceptualization and supervision.

Declaration of Competing Interest

The authors declare no conflict of interest.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.tca.2022.179407.

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