



## Feature Article

## Effects of nanoparticles on the morphology of immiscible polymer blends – Challenges and opportunities

Martina Salzano de Luna<sup>a,b</sup>, Giovanni Filippone<sup>a,\*</sup><sup>a</sup> Department of Chemical, Materials and Production Engineering (INSTM Consortium – UdR Naples), University of Naples Federico II, P.le Tecchio 80, 80125 Naples, Italy<sup>b</sup> Institute of Polymers, Composites and Biomaterials, National Research Council, P.le Fermi, 80055 Portici, NA, Italy

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## ABSTRACT

Adding small amounts of nanoparticles is an effective way to manipulate the morphology of immiscible polymer blends. However, although diffusely recognized, the potential of such an approach remains largely untapped. One of the reasons is the lack of fundamental understanding of the mechanisms that determine the nanoparticle-induced morphology alterations. This feature article addresses this topic, reviewing the recent literature and providing the authors' perspective on the future trends. The first part of the work is dedicated to the analysis of the effects of nanoparticles on the size, shape and stability over time of the polymer phases. Specifically, nanoparticle-induced phenomena such as morphology refinement, coarsening, formation of irregularly shaped domains, promotion of co-continuity, and morphology stabilization are critically discussed. In the second part, the perspectives of a clever employ of nanoparticles in polymer blends of technological interest are illustrated. Particular attention is paid to the strategies for valorizing biopolymers and recycled plastics, whose inherently scarce performances might greatly benefit from the approaches revised in this paper.

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\* Corresponding author.

E-mail address: [gfilippo@unina.it](mailto:gfilippo@unina.it) (G. Filippone).<http://dx.doi.org/10.1016/j.eurpolymj.2016.02.023>

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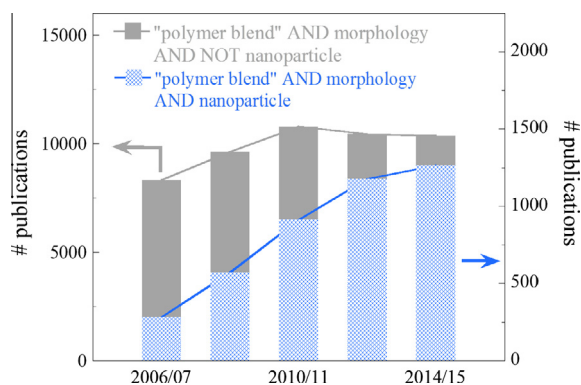
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## 1. Introduction

Polymers are typically immiscible because of unfavorably low mixing entropy. As a result, when two polymers are blended, they usually acquire a small-scale arrangement of the phases which is referred as “microstructure” [1]. From a phenomenological point of view, the morphology of immiscible polymer blend is the outcome of a typical sequence of events occurring during the melt mixing step [2–5]: (i) the shear and elongational stresses peel off the softened polymer from the surface of the pellets forming ribbons and sheets; (ii) these sheets get thinner under strain until a critical thickness is reached, and then capillary wave instabilities lead to the formation of holes; (iii) the second component coalesces through these holes; (iv) during further mixing, the pierced sheets become unstable and break into irregularly-shaped domains, whose further evolution determines the final blend morphology. Normally, the deformed volumes retract back to spherical shapes or break up driven by Rayleigh-type instabilities. As a result, drop-matrix morphologies commonly form. In principle, the toughness and impact resistance of such blends can result improved, but settling for such a result is definitely constraining. Actually, the spectrum of properties that could benefit from morphologies based on non-spherical domains is much wider. To give some examples: the barrier properties significantly improve in case of lamellar morphologies; the processability enhances in case of fiber-matrix microstructures, which also ensure low thermal expansion coefficient; the thermo-mechanical resistance and electrical conductivity greatly increase if the blend exhibits a co-continuous microstructure [6]. Therefore, if one aims at a clever manipulation of the blend morphology, one of the challenges is promoting and preserving non-spherical domains in the melt state. The approaches traditionally adopted for this purpose can be divided in two categories: (i) those based on the control of the kinetics of the mixing process; (ii) those aiming at the improvement of the affinity between the polymers. The former strategy basically consists in quenching non-equilibrium morphologies, which can be promoted through the use of specific dies [7–10] or via chaotic mixing [11–14]. Alternatively, one can exploit the changes in the rheology of the polymer phases during processing so as to preserve the transient morphologies which form at certain stages of the melt mixing. Such an approach has been especially studied to promote co-continuous morphologies [15] and refs. therein]. Consider now the second category. The inherent propensity of deformed domains to retract back to spherical shapes can be mitigated by adding a compatibilizing agent. The latter are macromolecular species usually based on a blocky structure, which can be either pre-made (physical compatibilization) or generated *in-situ* during the blending process (reactive compatibilization). The constitutive blocks of the compatibilizer are selectively miscible with the blend components. As a result, compatibilizers accumulate at the polymer–polymer interface and lower the interfacial tension [16]. In addition, provided that each block penetrates the parent phase deeply enough to be entangled with the constitutive chains, compatibilizers also enhance the interfacial adhesion; this aspect is crucial for an effective manipulation of the blend morphology through viscous stresses [17].

Although effective, the previous strategies suffer for scarce versatility, which can make them unaffordable in modern industrial contexts. After all, both approaches envisage the modification of the rheological and/or interfacial properties. Since the latter are both radically altered in the presence of nano-sized fillers, a clever use of nanoparticles offers an elegant way to manipulate the space arrangement of the polymer phase at the micron-scale without the need for substantial modifications of the mixing processes and/or investments in new chemistry. Such an approach has received a great deal of interest in recent years. As shown in Fig. 1, the number of publications addressing the morphology in nanocomposite polymer blends has steadily increased in the last decade; in contrast, the research on nanoparticle-free polymer blends has significantly slowed down in the same period.

Nevertheless, the mechanisms underlying the effects of nanoparticles on the microstructure of immiscible polymer blends still remain controversial. The present feature article systematically addresses this topic, reviewing the recent literature and providing the authors’ perspective on the future trends. The paper is structured as follows: the effects of nanoparticles on the size and shape and stability of the polymer domains are widely discussed in Section 2; per each topic, the different modes of action of nanoparticles accumulated in either of the polymer phases or at the polymer–polymer interface are highlighted separately. Finally, the technological implications are discussed in Section 3, in which notable cases of profitable employ of nanoparticles to improve the performances of immiscible polymer blends are collected. Particular attention is devoted to the valorization of low-environmental impact plastics, such as biopolymers and recycled plastics. In our opinion, this is the field in which the benefits stemming from nanoparticle-induced morphology alterations are already at the fingertips.



**Fig. 1.** Evolution of the number of publications in the last decade concerning the morphology of unfilled (left axis) and nanoparticle-filled (right axis) polymer blends. Source: [www.scopus.com](http://www.scopus.com) (accessed on January 2016).

## 2. Nanoparticle-induced effects on the morphology of immiscible polymer blends

### 2.1. Controlling the size of the phases

#### 2.1.1. Morphology refinement

Morphology refinement is probably the most renowned consequence of adding nanoparticles to immiscible polymer blends. In recent years the literature on this topic has significantly increased, but most of the times the conclusions which have been drawn were ambiguous and/or system-specific. When morphology refinement is the goal, many questions must be addressed: which kind of nanoparticles is the most effective? Is interfacial-localization to be preferred, or should one aim at promoting nanoparticle assembly inside either of the phases? And, in the latter case, is it better that the filler resides in the matrix or in the droplets? Aim of this section is reviewing the main mechanisms of morphology refinement, possibly identifying the ones that allow to minimize the amount of nanoparticles required to promote refinement. Let us start our analysis by considering the case in which the filler enriches either of the bulk polymers.

**Nanoparticles in the bulk phases.** Morphology refinement has been observed when the filler locates whether in the continuous or in the dispersed phase. In such cases, the refinement can be explained by invoking rheological arguments: changes in the viscosity ratio can alter the breakup/coalescence equilibrium in favor of the former. More precisely, since coalescence involves flows in both the drops and the matrix, an increased viscosity of either of the phases delays the merging process necessary for coalescence. The situation is particularly critical when the particles assemble in three-dimensional filler networks, as such structures drastically slow down the relaxation processes of the host phase. Nevertheless, many authors neglect the role of bulk rheology in the process of morphology refinement, proposing alternative physical mechanisms. Among others, the most common one is coalescence suppression: the nanoparticles dispersed in the matrix interpose themselves between colliding droplets preventing them from coalescing. Although invoked also in case of spherical fillers [18], simple geometrical arguments suggest that such a shielding mechanism could be particularly effective when plate-like nanoparticles are considered [19–22]. The effect can result accentuated if the filler is assembled in three-dimensional networks that trap the droplets of the minor phase [23]. It is important to observe that the effect of the filler embedded in either of bulk phase may be difficult to distinguish from that of particles gathered in the proximity of the drop-matrix interface. Ambiguities emerge especially when dealing with high aspect ratio nanoparticles, such as carbon nanotubes (CNTs). For example, Bose et al. invoked coalescence suppression in the presence of CNTs dispersed in the matrix phase of their blends, but transmission electron microscopy (TEM) reveals that portions of nanotube accumulated in the proximity of the interface protrude also inside the droplets [24]. Guo et al. ascribed the morphology refinement to the increased viscosity of the droplets containing CNTs, but the TEM pictures reveal that the particles exceed the contours of the drops [25]. In similar cases, ascribing the refinement to bulk or interfacial effects is difficult. Recently, Chen et al. ingeniously exploited both mechanisms by using a mixture of hydrophilic and hydrophobic nanoparticles: the former locate in the matrix phase causing an increase in its viscosity; the latter accumulate at the drop-matrix interface providing the drops with a shell against coalescence [26].

**Nanoparticles at the polymer-polymer interface.** Nanoparticles accumulated at the polymer-polymer interface are particularly effective in refining the microstructure of immiscible polymer blends. The underlying mechanisms are still controversial, but two main arguments are most commonly invoked: compatibilizing action and effects on the interfacial rheology.

Nanoparticles have been often proposed as a viable alternative to traditional copolymer compatibilizers [27–29]. The latter play a threefold role: (i) lower the interfacial tension between the polymers,  $\gamma_{ij}$  (emulsifying action); (ii) improve the interfacial adhesion; (iii) suppress coalescence. Janus nanoparticles apart, whose amphiphilic nature make them similar to chemical compatibilizers [30], common nano-sized fillers gathered at the polymer-polymer interface are proposed to play

one or more of the previous roles. The filler-induced lowering of the interfacial tension is often conjectured from the effects that a reduction of the interfacial tension would imply, e.g. a refinement of the average size of the dispersed polymer phase [21,31] or the merging of the two  $T_g$ s of the two polymers into one [32]. Actually, direct or indirect measurements proving an effective reduction of  $\gamma_{ij}$  in the presence of interfacially-adsorbed nanoparticles are seldom provided [18,33–35], and recent results question the emulsifying ability of the filler [36–38]. The issue is not trivial, and the concept of interfacial tension itself has to be redefined in the presence of a third particulate phase. Since interfacially-adsorbed particles reduce the actual liquid–liquid interface, Levine and Bowen theoretically derived an effective interfacial tension lower than the one measurable in the absence of particles [39]. In contrast, Vignati et al. experimentally proved that the interfacial tension in Newtonian emulsions is not affected by interfacial adsorption of particles [40]. To sum up, the actual emulsifying ability of nanoparticles in polymer blends remains an open issue, and contrasting opinion still exist even in the simpler case of Newtonian liquids.

Another action that “compatibilizing nanoparticles” should ensure is the improvement of the interfacial adhesion. Excluding the case in which the filler catalyzes interfacial chemical reactions, stronger interfacial interactions establish in case of simultaneous adsorption of the two polymers on the nanoparticles surface. The inherently amphiphilic feature of graphene oxide or properly functionalized multiwalled CNTs promotes polymer adsorption [41,42]. However, simultaneous chemical adsorption seems not strictly necessary in the case of organo-clays, which may exhibit coupling ability even if one or both of the polymers exhibit scarce affinity with the particles [43]. The idea is that intercalation of the polymer(s) in the inter-layer galleries of interfacially-located clay stacks plays the same role as a strong adsorption on the platelet surface. The non-specificity of such a coupling mechanism was emphasized by Rafailovich and co-workers, who proposed the employ of organo-clays for compatibilizing recycled blends with uncertain composition [28,44].

The third action expected from interfacially-adsorbed nanoparticles with actual compatibilizing efficiency is that of coalescence suppressor. Compared to the other two, such an ability is commonly recognized in many different systems, being generally ascribed to steric hindrance effects: the nanoparticles act as a physical barrier that prevents the direct contact between drops of the minor phase [45–48]. High steric hindrance ability is expected in case of interfacial saturation, which could be easier to achieve with flexible, plate-like nanoparticles [44]. However, suppressed coalescence has been reported also in the case of partial coverage with nanotubes [37]. Another phenomenon that stabilizes against coalescence is “drop clustering”, i.e. the formation of stable bunches of droplets bridged together via shared layers of particles [49,50]. Such a mechanism, which occurs when the drop surface is not fully covered, will be discussed in more detail in Section 2.3.

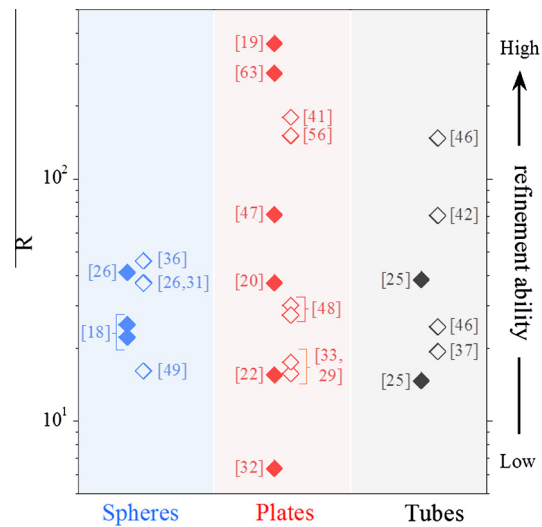
As an alternative to compatibilization arguments, several authors ascribe the morphology refinement in the presence of nanoparticles to alterations in the interfacial rheology. In principle, a filler-induced reduction of the mobility of the interface slows down the drainage process of the film of continuous phase between pairs of droplets, thus hindering coalescence. The literature on the rheology and dynamics of particle-laden interfaces has been recently reviewed by Mendoza et al. [51]. Among others, it is worth mentioning the studies by Vermant, Moldenaers and co-workers, who investigated the relationships between the interfacial structures of particle monolayers and the rheological response [52]. The stabilization mechanism against coalescence in polymer blends is ascribed to the modification of the rheological properties of the interface by a mechanism similar to that occurring in Pickering emulsions, i.e. Newtonian emulsions stabilized by interfacially-adsorbed particles [53]. In this sense, nanoparticles act in a different way from block copolymers, which mainly reduce the interfacial tension. Essentially the same conclusions were drawn by Lebaume et al., who focused on the marked viscous connotation and long relaxation time of clay-armored polymer–polymer interfaces [54], and by Moghimi et al., who assigned to a nanoparticle-induced drop clustering phenomenon a key-role in suppressing coalescence [49].

Before moving to the next Sections, the refinement ability of different kinds of filler is compared. For this purpose we introduce an efficacy parameter  $R$ , defined as the percentage reduction of the number average drop size normalized over the amount of nanoparticles (in wt%) responsible for the refinement. The values of  $R$  estimated for the cited papers in which the number average drop radius was available are shown in Fig. 2; the data are classified in terms of shape of the nanoparticles and preferential localization within the blend.

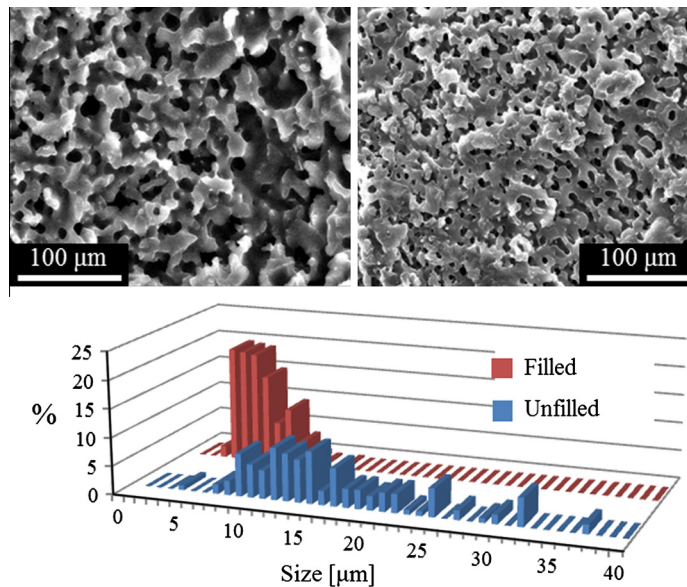
Although the limited number of data concerning nano-tubes and nano-spheres makes it difficult to draw unambiguous conclusions, the comparison reveals that plate like nanoparticles are generally more effective in promoting refinement. Interestingly, the bulk or interfacial localization of the filler seems not to be a critical aspect. Therefore, one can conjecture that compatibilizing effects, which are specific for interfacially-adsorbed particles, play a minor role compared to rheological aspects and shielding mechanisms, which instead prescind from filler localization. Systematic studies on this subject are necessary to support such a conclusion.

**2.1.1.1. Refinement of co-continuous microstructures.** To conclude this survey of the recent literature on nanoparticle-induced morphology refinement, it is interesting to observe that the phenomenon takes place also in blends with co-continuous morphology. An example is given in Fig. 3, where the effect of 0.5 wt% of graphene nanoplatelets (GNPs) on the characteristic size of the phases of a co-continuous blend of polystyrene (PS) and poly(ethylene oxide) (PEO) is shown.

Unless rare exceptions [55,56], the refinement of co-continuous morphology is often merely noticed, the attention being focused on other effects related to the presence of nanoparticles. To give some examples, clear morphology refinements can be noticed in [57,58], but the authors address the possibility of reducing the percolation threshold of conductive fillers via selective interfacial localization; a drastic refinement was shown also in [59], but in this case the focus is on the shift in the onset of phase co-continuity. Actually, the refinement of co-continuous morphologies can have a relevant impact on the mechanical and transport properties of the blends, and the potential offered by a focused employ of nanoparticles should



**Fig. 2.** Refinement efficacy parameter estimated for the papers cited in Section 2.1.1 in which the number average drop radius was available. Empty symbols refer to interfacially-adsorbed nanoparticles, while filled ones are for nanoparticles residing in the bulk phases. The references are reported in square brackets in proximity of the data.



**Fig. 3.** Scanning electron microscopy pictures of PS/PEO (50/50 wt/wt) unfilled (a) and filled with 0.5 wt% of GNPs (b), and normalized distribution of the characteristic size of the polymer domains (c). Unpublished results.

deserve greater attention. The authors of the present paper have recently explored the possible advantages of such a strategy. In particular, nanoparticle-assisted morphology refinement was exploited in [60] for improving the dispersion of hydrophilic nanoparticles (ZnO) in a hydrophobic matrix through a template-based strategy. In another paper, positive deviations from the expectations of mechanical models were linked to a better stress transfer between the refined polymer phases of the co-continuous blend [61].

### 2.1.2. Morphology coarsening

Compared to the vast literature on refinement, experimental studies reporting nanoparticle-induced coarsening of microstructure are definitely less abundant. In addition, the increase of the average size of the dispersed phase is often noticed without being explained. Nevertheless, the phenomenon is well documented, and it cannot be neglected if one aims at a focused design of nanoparticle-containing polymer blends. Here we mainly focus on those papers in which a physical

interpretation of the coarsening is provided. We highlight that the study of the coarsening processes over time is not addressed here but in Section 2.4, where the stabilization ability of nanoparticles is analyzed.

*Nanoparticles in the bulk phases.* As for morphology refinement, coarsening was reported in case of nanoparticles either located in the bulk phases or accumulated at the interface. The first category is richer, and rheological arguments are generically invoked to explain the phenomenon. Opposite effects on the size of the dispersed phase were sometimes noticed depending on whether the particles accumulate in the matrix or drop phase. Coarsening is more frequently observed when the filler enriches the drops, being usually ascribed to the increase in the viscosity of the dispersed phase [47,62–65]. Among others, Kong et al. also noted that the reduced deformability of filled droplets may bring about a higher efficiency of the collisions at the origin of coalescence [66], whereas Guo et al. highlighted the role of the aspect ratio of the nanoparticles, observing that the domain size gets larger to accommodate long nanoparticles such as CNTs [25]. The interpretation is rather vague when coarsening takes place with the particles accumulated in the matrix phase [67,68]. Tong et al. proposed that clusters of nanoparticles form in the matrix film trapped between approaching droplets due to confinement effects; when such aggregates migrate towards the matrix driven by thermodynamics, the drainage of the film between the droplets is favored and, hence, coalescence is favored [50].

*Nanoparticles at the polymer-polymer interface.* Let us consider now the case of nanoparticles accumulated at the polymer-polymer interface. Xiu et al. reported an unexpected increase of the size of drops in the presence of high amounts (15 phr) of TiO<sub>2</sub> nanoparticles [69]. The authors ascribed this finding to the strong self-networking ability of the nanoparticles, referring to future works for further investigations. More targeted studies on systems with a selective interfacial localization of the filler were performed by Velankar and co-workers. Two mechanisms were conjectured depending on which phase preferentially wets the (spherical) particles: (i) when the particles have better affinity with the drop phase, coarsening is due to a bridging-dewetting mechanism reminiscent of particle-induced coalescence of bubbles in foams [70]; (ii) when the affinity with the matrix prevails, and the particles do not entirely cover the drop surface, coalescence may take place under flow conditions because the drops are held in close proximity via particle bridging [71]. Concerning the latter mechanism, some coalescence can be inferred from Fig. 8 in [49] for samples sheared under relatively high stresses, but the authors do not discuss this finding.

*2.1.2.1. Coarsening of co-continuous microstructures.* As far as co-continuous blends are concerned, to the best of our knowledge only Lee et al. reported some nanoparticle-induced coarsening in as-prepared samples [72], but the authors did not comment on this experimental evidence. Such a lack in the literature is likely due to the fact that most of the studies focus on the use of nanoparticles for the stabilization of co-continuous morphologies, notoriously inclined to quickly coarsen over time. This topic is specifically addressed in Section 2.4.

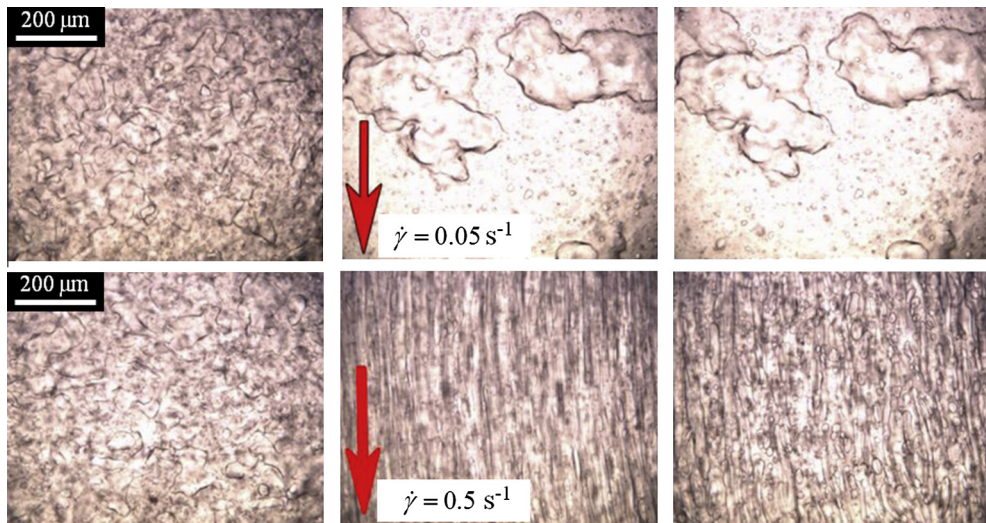
## 2.2. Manipulating the shape of the phases

The morphology of unfilled blends under quiescent conditions is dictated by the minimization of the interfacial tension. As a result, deformed domains retract back to the spherical shape in a characteristic time that basically depends on the ratio between the blend viscosity and interfacial tension [73,74]. Since nanoparticles affect both these parameters, a divergence of the shape relaxation times can be in principle induced upon filling. In other words, stable non-spherical shapes can be promoted by simply adding nanoparticles. Actually, the spectrum of possibilities is wider: polymer drops can be glued, form non-coalescing clusters, chains, or they can stably assume grotesque shapes by means of simply addition of small amounts of nanoparticles. The possibility of controlling the shape of liquid drops is highly attractive, and the degree of control of the morphology has reached noticeable levels in the field of low-viscosity emulsions [75] and refs. therein]. The current state of the art for immiscible polymer blends is presented below.

### *Nanoparticles in the bulk phases*

An effective way to make the polymer domains unable to relax consists in filling them with nanoparticles, so as to impart them an appreciable yield stress. The potentialities of such an approach were shown for low-viscosity emulsions by Pawar et al., who were able to fabricate anisotropic structures of partially crystalline shapes by arrested coalescence of three or more droplets with internal microstructure [75]. Frostad et al. found that the mechanism of drop adhesion is based on the formation of capillary bridges, and the adhesive force was measured to be on the order of few tens of  $\mu\text{N}$  [76]. As far as high viscosity polymer blends are concerned, Kong and co-workers recently showed the striking shape stability over time of polymer domains containing inside even low amounts of nanosilica [66]. The authors investigated low and high capillary numbers, so as to favor coalescence and break up, respectively.

The nice micrographs of the resulting irregularly-shaped big domains and fibrils prove that the shape remains essentially unaltered up to one hour after the flow was stopped (see Fig. 4). Liu et al. stressed the role of nanoparticle networking for the stabilization of the host domains, whose shape relaxation is hindered because of the reduced mobility of the polymer chains [77]. A different mechanism was conjectured by Xiu et al.: the strong networking ability of nanosilica particles protruding from the host domains causes the filled drops to partially coalesce, giving rise to “network-like structures” based on discrete and yet irregularly-shaped domains [78]. The same authors benefited from the branched feature of the network-like

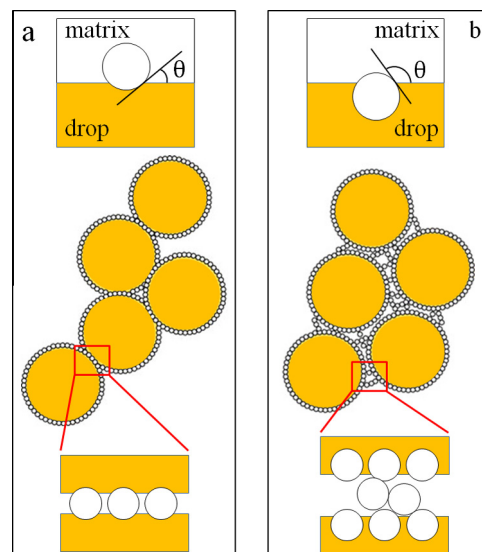


**Fig. 4.** Optical micrographs showing irregularly-shaped silica-filled polyamide 6 domains in a PS matrix. Left column: initial morphology. Center column: after shearing at low (upper row) and high (bottom row) shear rate for 4000 s. Right column: after quiescent relaxation for 3600 s. The arrows indicate the flow direction. Readapted from [66].

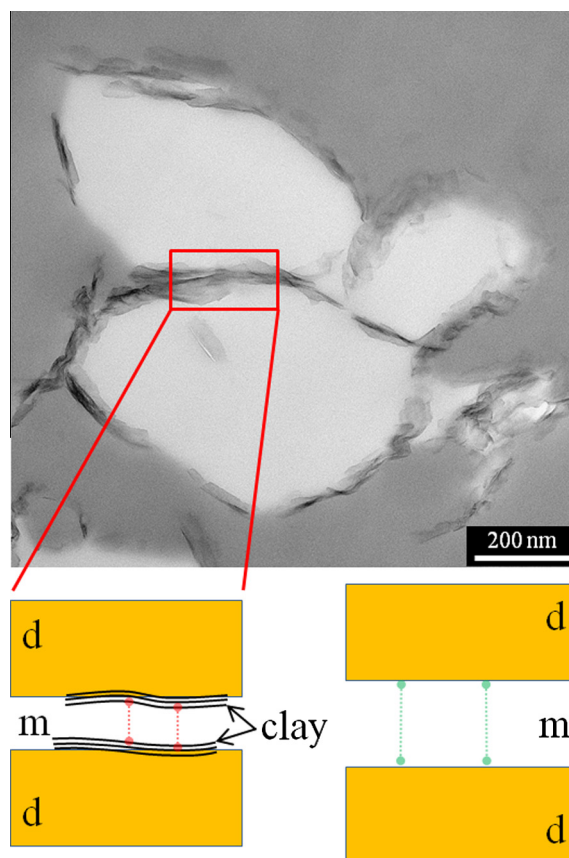
structure to lower the electrical percolation threshold of conductive carbon black particles [79]. Finally, Lee et al. noticed irregular domains of the minor phase in the presence of nanoparticles located in the matrix phase [20]. The authors ascribed the elongated shape of the drops to their confinement between clay platelets aligned in the matrix because of the flow field experienced in the course of processing.

#### *Nanoparticles at the polymer-polymer interface*

The shape of polymer domains can be manipulated by coating them with nanoparticles. The latter profoundly alter the interactions among the drops of dispersed phase, which may either stick together or partially coalesce giving rise to irregularly-shaped domains. The possibility of “gluing” liquid drops by means of interfacially-adsorbed particles can be exploited to stabilize low-viscosity emulsions [80,81]. Vermant et al. [45] and Thareja and Velankar [82] noticed a similar phenomenology in immiscible polymer blends. In both cases the filler consisted of silica nanoparticles, which are roughly spherical in shape and accumulate at the interface, protruding towards the matrix due to a higher affinity with it. Under such circumstances, a monolayer of particles that bridges a pair of drops allows to satisfy the equilibrium contact angle condition at two polymer-polymer interfaces simultaneously (see Fig. 5a). The stability of such a configuration results in



**Fig. 5.** Schematic of the clustering mechanisms when the particles are preferentially wetted by (a) the matrix and (b) the drop phase. Readapted from [85].



**Fig. 6.** Cluster of clay-coated PMMA drops (d) in a PS matrix (m). The clustering mechanisms proposed in [86] is depicted in the cartoon: the attractive interaction between clay-coated drops (red connectors) is estimated to be 2 orders of magnitude higher than that between bare drops (green connectors). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

non-coalescing clusters/chains of polymer droplets, which provide the blend with a weak gel-like behavior [83,84]. The effect of the particle content was investigated by Velankar and co-workers: at low filler loadings the particles preferentially accumulate in the bridge region; at high particle loadings the entire surface is nearly covered, the drops appear faceted, and the morphology resembles a foam structure [71].

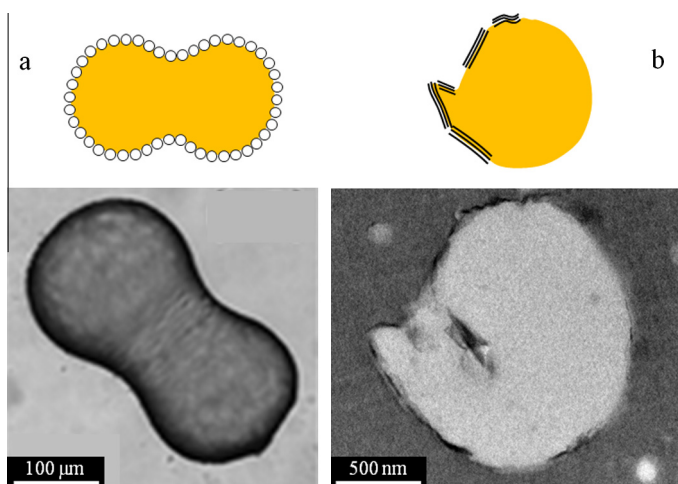
The strongly-held opinion that drop clustering can occur only when the particles prefer the matrix phase has been recently called into question by Zou et al. [85]. Together with usual drop bridging, the authors unexpectedly noticed drop clustering also when the interfacially-adsorbed nanoparticles are preferentially wetted by the dispersed phases. Such a finding was explained by invoking the noticeable propensity to flocculation of nano-silica, which promote the bridging of completely covered drops subjected to a slow shear flow without the needing of shared monolayers of nanoparticles (see Fig. 5b).

Interestingly, Filippone and Acierno came to the same conclusions by dealing with a completely different system, i.e. a blend of PS and poly(methyl methacrylate) (PMMA) filled with small amounts of organo-clay selectively located at the drop-matrix interface [86]. The phenomenon clearly emerges from the TEM micrographs, in which non-coalescing clay-covered droplets are easily recognizable (see Fig. 6).

The authors estimated that the attractive force between coated drops is two orders of magnitude higher than in the absence of nanoparticles. As a result, coated droplets which come into contact during slow shear flows tend to stick together forming clusters. In addition, the clustered drops appear evidently distorted even after long time in the melt state in quiescent conditions. It is important to observe that clay-induced irregularly shaped domains do not necessarily reflect interfacial saturation, which is instead required with spherical nanoparticles. The mechanism generally invoked in such cases is known as “arrested coalescence”: the drops remain frozen in an intermediate shape because particle jamming offsets the Laplace pressure driving force for coalescence (Fig. 7a) [87]. Differently, the inherent bending stiffness of clay platelets lying on the drop surface locally frustrates shape relaxation even in case of partial coverage (Fig. 7b). Macosko and coworkers recently invoked a similar mechanism also for co-continuous blends [56].

Surprisingly, the intriguing opportunity of manipulating the blend morphology irrespective of interface saturation by means of plate-like nanoparticles has received scarce attention. One possible explanation is that the literature on interfacially-adsorbed particles is dominated by Pickering emulsions, which are mainly based on spherical particles. The



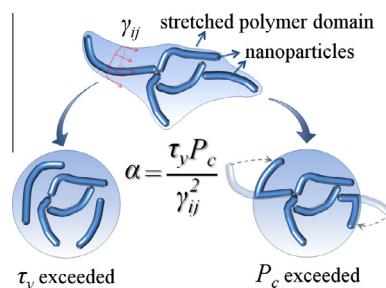


**Fig. 7.** Examples of irregularly-shaped drops: (a) oil drop in water stabilized by interfacial jamming of spherical silica particles; (b) PMMA drop in PS stabilized because of the bending stiffness of clay platelets partially coating the drop surface. The optical micrograph in (a) is Readapted from [87].

morphology of such systems is mainly dictated by contact angle considerations, which are hard to be invoked in case of plate-like nanoparticles. Nonetheless, if the goal is manipulating the shape of the polymer domains, simple geometrical considerations suggest not to neglect the possibilities offered by this kind of fillers, which better adapt to the inherent two-dimensional feature of the interface. Note that interface-located mono-dimensional nanoparticles seem not to guarantee the same effect: very recent results indicate that CNTs do not preserve irregular shapes of the polymer phases unless saturate the interface [88].

### 2.3. Alteration of the co-continuity interval

The exceptional stability of non-spherical polymeric domains can result in their merging in the contact points, thus favoring the formation of co-continuous morphologies. This kind of microstructure has attracted a great deal of interest in the recent past as the interpenetration of the phases can result in a synergistic combination of the properties [15]. Regarding co-continuous blends containing nanoparticles, the first studies mainly concerned electrically conductive fillers, whose percolation threshold can be significantly reduced by promoting their confinement in either of the phases or at the polymer-polymer interface [89–92]. Such an opportunity captured most of the attention of the researchers, who rarely focused on the effect of the filler on the blend morphology. Gubbels et al. and Steinmann et al. were among the first to notice that the range of full co-continuity gets broader in presence of nanoparticles [93,94]. It was immediately clear that simple rheological models uniquely based on the viscosity ratio [95–97] were not able to predict the co-continuity range in the presence of nanoparticles. However, the reasons for such inadequacy remain unclear [98,99], and many authors keep referring even now to such models to account for nanoparticle-induced alterations of the co-continuity interval [100–104]. The matter is actually complex, and Pawar and Bose recently discussed the main mechanisms through which nanoparticles promote “peculiar morphologies” in immiscible blends [105]. The authors focus on the roles of reduced interfacial tension and retarded relaxation in the morphological alterations. Concerning the former aspect, although frequently invoked to explain morphology refinement of drop-matrix morphologies (see Section 2.1), it is seldom used to explain the ability of nanoparticles of promoting co-continuity [106]. Rheological arguments are generally preferred, and one of the authors of this paper carried out a series of systematic studies. In [23,107] the unexpected appearance of co-continuity in blends with unbalanced composition (75/25 wt/wt) was ascribed to the slowed relaxation dynamics of the nanoparticle-rich polymer phase, which preserve the co-continuous morphology attained during melt mixing. The kinetic factors controlling the uneven distribution of nanoparticles in highly viscous polymer blends were exploited in [108], where the possibility of promoting co-continuity by acting on the melt-compounding procedure was investigated. The selective localization of the nanoparticles in either of the bulk polymers is not strictly necessary, and also interfacially-localized fillers were proved to be effective [59]. In particular, it was found that plate-like nanoparticles affect the blend morphology much more than spherical ones, which suggested that interfacial rheology may play a major role in the phenomenon of nanoparticle-induced co-continuity. The previous studies paved the way for a systematic investigation of the interplay among bulk rheology, interfacial tension, and stiffness of the nanoparticles, which were identified as the more relevant parameters responsible for morphological alterations in nanofilled blends. In detail, the interfacial tension  $\gamma_{ij}$  drives the domain to retract back to a spherical shape; the relaxation process cannot take place unless exceeding either the yield stress of the filler network inside the polymer domain,  $\tau_y$ , or the critical buckling load of the nanoparticles constituting the network,  $P_c$ . Such parameters were combined in a single dimensionless group  $\alpha$ , which expresses the ability of a certain kind of nanoparticles to keep a host polymer domain deformed, eventually



**Fig. 8.** Schematic of the mechanisms through which a stretched domain containing nanoparticles can lose its elongated shape. Readapted from [109].

promoting co-continuity (see Fig. 8) [109]. The idea was corroborated through comparative analyses carried out on blends containing different kinds of nanoparticles, but further experimental validations on different systems would be particularly appreciated.

Rather than on rheology, many authors focus their attention on the self-networking ability of the nanoparticles. Actually, the two aspects are strictly interrelated, and studying them separately is challenging. While not denying the relevance of rheology, Xiu et al. recently ascribed to nanoparticle self-networking the key-role in driving the blend morphology [78,110]. Wu and co-workers pushed this concept even farther, proposing that the nanoparticles drag the domains of the wetting polymer while self-assembling, thus causing their welding in a co-continuous structure [111]. To support this idea, in [112] the same group observed that the nanoparticles that tend to form separated clusters instead of three-dimensional networks have the opposite effect of breaking down the continuity of the host polymer phase. In our opinion, the previous physical picture suffers from several weak points. First of all, even supposing that the nanoparticle self-assembly is the only responsible for the space arrangement of the polymer phases, we argue that the typically high viscosities of polymer melts and relatively low thermal energy of flocculating nanoparticles make questionable the assumption of dragging of micrometric polymer domains. More realistically, the fine filler distribution ensured by intense mixing, coupled with the preferential wetting of one of the polymers, refines the space arrangement of the minor phase, whose merging in the contact points eventually results in fine co-continuous morphologies. Two arguments support this picture: first, a bad nanoparticle dispersion may result in the loss of co-continuity even in the presence of filler networks [113,114]; second, single-step mixing procedures, which promote uniform distribution of the filler, have been found to be more effective than two-step ones, in which the particles are often confined in only one of the polymer phases [78,108]. Furthermore, assigning to nanoparticles dynamics the key-role in driving the blend morphology means totally neglecting the other side of the coin: the filler is in turn subjected to the anchoring/dragging forces exerted by the polymer phases in the course of their natural morphological evolutions. Fu and co-workers were among the few to account for the interplay between polymer phase-separation and preferential adsorption of one of the polymers on the nanoparticle network [115].

The main effects of nanoparticles on the co-continuity of polymer blends are summarized in Table 1 for the papers cited in this Section. The data are classified in terms of shape of the nanoparticles and observed phenomenon.

Finally, we would like to mention other two mechanisms through which nanoparticles may induce alteration of the co-continuity interval. The first one, specific for CNTs, was proposed by Pötschke and co-workers: because of their large size, the nanotubes may bridge the polymer phases, thus stabilizing the co-continuous structures that transiently form during melt mixing [116]. The second mechanism is based on the phenomenon of nanoparticle-induced drop clustering described in Section 2.2. As shown in Fig. 9, the interconnection of the domains of the minor phase can eventually result in co-continuity. Compared to a bridging-dewetting mechanism [70], which simply causes drop coalescence, here the domains remain elongated due to the pinning exerted by the clay particles at the drop surface. Preliminary analyses suggest a certain relevance of such a phenomenon, which is currently the subject of investigation by our group.

#### 2.4. Morphology stabilization over time

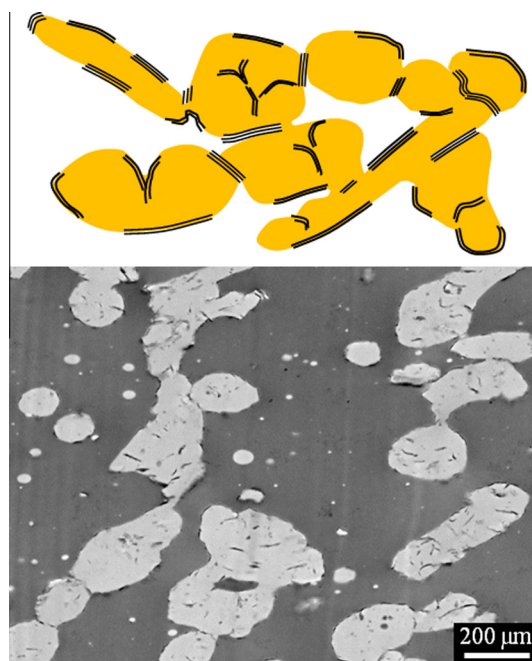
The morphology of immiscible polymer blends produced through melt mixing is usually in a non-equilibrium state. As a consequence, the frozen-in phase morphology quickly evolves when the blend is melted again. This happens quite frequently in industrial contexts, in which the materials can experience multiple melt processing steps. Since the microstructural changes proceed in an uncontrolled way, they are generally unwanted. Again, nanoparticles represent a feasible solution for stabilizing the blend morphology either during flow or in quiescent conditions.

##### 2.4.1. Stabilization during flow

Small amounts of nanoparticles are known to substantially reduce the sensitivity of the blend microstructure to shear flows [24,45,117]. Such stabilizing action depends on the localization of the filler, which is particularly effective in case of interfacial positioning. Vermant et al. observed that interfacially-adsorbed silica nanoparticles stabilize drop-matrix morphology of 30% poly(isobutylene) (PIB) in 70% poly(dimethylsiloxane) (PDMS) or vice versa. The effect was not symmetric,

**Table 1**  
Effects of nanoparticles on the co-continuity of immiscible blends.

Filler		Anticipation and/or broadening of the onset of co-continuity		Unexpected formation of co-continuous morphology	
Shape	Type	Refs.	Extent of anticipation (wt%)	Refs.	Blend composition (wt/wt)
Spheres	Carbon black	[93]	15	[106]	40/60
		[93]	25	[110]	85/15
	Glass spheres	[94]	–	[111]	60/40
		[101]	10	[111]	70/30
		[112]	10	[111]	80/20
Plates	Clay	[59]	15	[23]	75/25
		[108]	5	[99]	50/50
	[108]	10	[103]	40/60	
	Sepiolite	–	–	[104]	40/60
		–	–	[107]	75/25
–		–	[109]	70/30	
Tubes	MWCNT	–	–	[115]	60/40
		–	–	[99]	30/70
		–	–	[100]	50/50
		–	–	[102]	50/50
		–	–	[109]	70/30
–	–	[113]	50/50		
–	–	[114]	60/40		
–	–	[109]	70/30		



**Fig. 9.** Drop clustering promoted by interfacially-adsorbed clay particles in a PS/PMMA blend (70/30 wt/wt) results in drop interconnection, thus favoring co-continuity. Note that the particles inside the PMMA bright domains mainly derive from the clustering of clay-coated drops. Unpublished results.

being more pronounced when PDMS is the matrix phase [45]. Such a finding was interpreted in the light of experiments performed by Stancik et al. on low-viscosity emulsions [118]: a water-in-oil emulsion is better stabilized by slightly hydrophobic particles, which protrude from the water drops and prevent coalescence during flow through a steric hindrance mechanism. Similarly, the silica particles in the Vermont's systems are more effective when the PIB represents the drop phase as they slightly prefer PDMS. Essentially the same mechanism was invoked by Tong et al., who additionally identified a second stabilizing phenomenon when low amounts of particles reside inside the matrix phase: non-coalescing clusters of

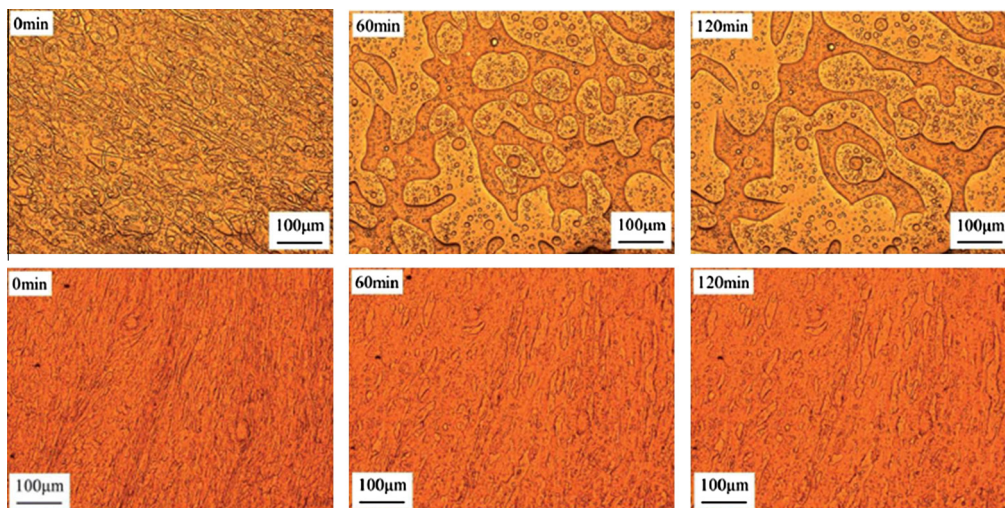
droplets form during shear flows as a consequence of nanoparticle-induced drop bridging [50]. On the other hand, Vermant et al. proved that coalescence can be completely suppressed even if almost no bridged droplets can be observed via scanning electron microscopy (SEM) images [84]. Contextually, the authors found that, besides the coalescence, also the breakup pattern is affected by the filler. Finally, it is important to observe that nanoparticles can also have the opposite effect of reducing the blend stability, promoting morphological changes under flow. Among others, Kong et al. [66] and Filippone and Acierno [86] noticed nanoparticle-promoted drop coalescence and drop clustering during slow shear flows.

#### 2.4.2. Stabilization in quiescent conditions

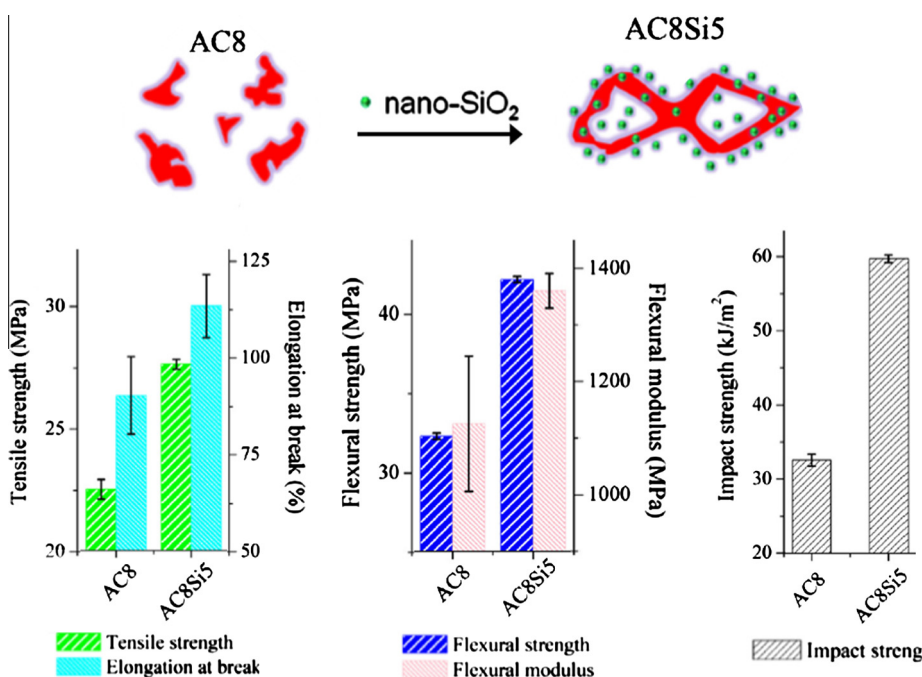
When a blend is subjected to quiescent post-treatments at temperatures above the softening/melting point of the polymeric constituents, its morphology evolves over time towards phase coarsening [119,120]. The phenomenon is especially evident in case of co-continuous blends, which are particularly unstable because of their high specific interface. Such a propensity to coarsening of co-continuous blends can be ingeniously exploited to obtain porous and/or gradient microstructures [121,122]. However, generally the goal is preserving fine morphologies. Gubbels et al. first reported that co-continuity in a blend of polyethylene (PE) and PS is stabilized during thermal annealing by carbon black selectively distributed in the PE phase [93]. Since an interface-active filler is expected to accumulate at the interface, the authors excluded that stabilization was due to a reduction of the interfacial tension. They instead ascribed coarsening inhibition to the increased viscosity of the host phase, which slows down the coalescence step. Similar conclusions were drawn for co-continuous blends containing other kinds of nanoparticles [88,101]. Yang and co-workers systematically addressed the effect of silica nanoparticles in a series of very recent papers [55,123,124]. Whether the nanoparticles preferentially reside at the polymer-polymer interface or they enrich one of the phases, the coarsening process slows down with increasing the filler content, being completely suppressed at high loadings. Two coarsening patterns characterize the morphological evolution of co-continuous unfilled blend: retraction of elongated domains and coalescence of the latter. Exploiting real-time microscopy observations, the authors found that the coalescence step is the one that is mainly affected by the presence of nanoparticles (Fig. 10).

When silica is segregated in one of the phases, the formation of a filler network also significantly contributes to inhibit the relaxation of elongated domains [123]. However, the latter mechanism is not itself essential for coarsening inhibition. Indeed, nanoparticles adsorbed at the interface of a blend having drop-matrix morphology suppress the coalescence process even though the filler does not form a percolating structure [124]. Macosko and co-workers focused on the stabilizing effect of interfacially-adsorbed clay nanoparticles on the morphology of co-continuous blends [56]. The authors found that coarsening takes place until the entire interface is covered by the filler. This suggests that interfacial jamming is the main mechanism responsible for the arrest of coarsening. Morphology stabilization is much less pronounced when the plate-like nanoparticles enrich the bulk phases. In this case the effect simply reflects the increased viscosity of the host phase, which slows down the coarsening rate.

Although less studied, coarsening during quiescent thermal annealing takes place also in case of distributed morphologies. Parpaite et al. investigated the stability of a drop-matrix blend filled with different kinds of silica nanoparticles [125]. Irrespective of its localization within the blend, the filler was found to inhibit coalescence during quiescent thermal annealing. Differently, the stabilizing efficacy of plate-like nanoparticles seems to be strongly dependent on their localization. Noticeable stabilization effects were observed when the filler enriches the continuous phase [19,126]. The effect was mainly ascribed to the barrier effect against coalescence provided by the lamellae. On the other hand, the stabilizing action was not confirmed when the filler accumulates in the dispersed phase [19,127].



**Fig. 10.** Morphology evolution of neat (top row) and filled (bottom row) blends observed by an optical microscope during quiescent thermal annealing. The presence of about 4 wt% of nanoparticles completely suppresses the phase coarsening. Readapted from [123].



**Fig. 11.** Simultaneous enhancement of toughness and stiffness due to nanoparticle-induced formation of an elastomeric framework inside the matrix. The scheme on the top highlights the nanoparticle-induced alteration of the blend morphology. The acronym AC8 refers to a poly(acrylonitrile–styrene–acrylic)/chlorinated polyethylene blend with 8 wt% of minor phase; the AC8Si5 one refers to the same blend in which 5 wt% of silica nanoparticles are added. Readapted from [133].

### 3. Properties and applications

The possibility of using nanoparticles to finely tune the microstructure of the polymeric domains paves the way for the production of materials having prescribed properties. The aim of this section is collecting some meaningful examples of polymer blends whose morphology was judiciously tailored through the addition of nanoparticles in order to obtain the desired set of macroscopic properties.

#### 3.1. Optimizing the mechanical and electrical properties

The mechanical and electrical behavior of nano-filled polymer blends has been largely studied in the past from both experimental and theoretical point of view. The literature in this field is abundant, and it has been recently reviewed elsewhere [27,128]. Here we limit ourselves to provide a brief overview of some notable papers in which nanoparticle-induced alterations of the blend morphology have been deliberately exploited to realize materials with a prescribed set of macroscopic properties.

A judicious control of the blend morphology can help in remedying the typical low toughness of nanocomposite polymer blends [21,129–131]. Among others, it is worth mentioning the studies by Zhang et al., who obtained a simultaneous improvement of stiffness and toughness thanks to the presence of an elastomeric framework induced by nanoparticles [132,133] (see Fig. 11).

Nanoparticle-induced co-continuity can also be exploited to improve the mechanical resistance at high temperature. The idea is using the filler to promote the space continuity of the phase having higher melting/glass transition temperature, so as to preserve the structural integrity of the blend even in case of melting of the second component. Following this strategy, Filippone et al. were able to prevent the softening of a sample at 75 wt% of high density PE (HDPE) at a temperature well above the melting temperature of that phase thanks to the presence of a continuous framework of clay-filled polyamide 6 (PA6) [23]. Yang et al. succeeded in the simultaneous improvement of the impact strength and electrical conductivity by manipulating the blend morphology through conductive fillers [134]. The formation of a space-spanning network of nanoparticles is the basic principle for the production of electrically conductive polymeric materials. The well-known mechanism of “double percolation” allows reducing the amount of filler necessary for percolation by promoting its confinement at the polymer–polymer interface. A clever upgrade of this concept was recently proposed by Cohen et al.: rather than trying to distribute the conductive filler at the polymer–polymer interface of a binary co-continuous blend, the authors promoted its confinement into an inter-phase of a minor third polymeric component, which was continuous throughout the blend [135].

### 3.2. Tuning the blend microstructure for templating purposes

The inherent phase segregation of polymer blends can be exploited as passive template for a wide variety of applications. The underlying idea is that one of the polymeric domains represents a sacrificial phase, whose removal allows producing a scaffold based on the second component with controlled porosity. In this context, nanoparticles can be profitably used to tune the blend morphology. As an example, Salzano de Luna et al. exploited a template-based approach to efficiently disperse hydrophilic nanoparticles within a hydrophobic polymer matrix [60]. The procedure envisages the permeation of a well-dispersed nanoparticle suspension inside a micro-porous HDPE matrix, which was obtained through the selective extraction of a sacrificial PEO phase from a finely co-continuous HDPE/PEO blend. In order to optimize the process, the HDPE scaffold should contain a thick network of tiny channels, i.e. the starting blend should exhibit a microstructure as fine as possible. Such a refinement was promoted by adding small amounts of organo-clay. Other examples of profitable employ of nanoparticles can be found in the field of polymer scaffolds for tissue engineering applications [136,137]. Among others, Baklavaridis et al. proved that the proper selection of the clay loading allows the fine tuning of degree of porosity and pore average diameter [137]. Similarly, Bose and co-workers produced antibacterial PE membranes for water purification from a PE/PEO blend filled with graphene oxide nanoplatelets, whose surface chemistry was properly modified to optimize the dispersion of PEO drops in the PE matrix [138,139].

### 3.3. Valorizing low-environmental impact plastics

Scientific breakthroughs and innovative solutions are continuously sought in the field of recycling, re-use, substitution of environmental impacting materials, and smarter design of biodegradable materials. In this context, we argue that nanoparticle-assisted morphology manipulation in blends partially or totally based on sustainable polymers might represent a viable route for enlarging the fields of application of such eco-friendly (and yet low-performance) materials. The recent advances achieved by means of such an approach in the field of (i) recycled petroleum-derived plastics and (ii) bioplastics are discussed below.

#### 3.3.1. Recycled petroleum-derived plastics

The use of nanoparticles to control the morphology and performances of blends of recycled plastics was first explored by Si et al. [28], who proposed that compatibility between polymers can be enhanced by melt mixing with small amounts of organo-modified clays. The generality of the proposed compatibilization mechanism makes such a strategy particularly attractive in the case of plastic wastes, which are frequently not well sorted. As a result, the mechanical properties of the resulting blends are usually unacceptably scarce. As an example, Andričić et al. showed that tensile strength and elongation at break of polyvinyl chloride (PVC) sheets dramatically decrease in the presence of a fraction of PVC waste contaminated with only 3 wt% of polypropylene (PP); nonetheless, an acceptable product containing up to 30 wt% of waste material can be obtained by simply adding small quantities of surface-modified nanoparticles of calcium carbonate [140]. Similarly, substantial improvements of the mechanical properties were reported for nano-filled blends based on recycled polyethylene terephthalate (PET) [141,142]. An alternative strategy was proposed by Causa et al., who used nanoparticles to valorize recycled PET reprocessed at low temperature. In more detail, the compounding step was carried out below the melting temperature of PET, which was therefore used as “solid filler” in a co-continuous HDPE/PP blend; the addition of small amount of nano-clay efficiently refined the blend morphology at the micron-scale, causing an improvement of the high-temperature mechanical resistance [143]. On the other hand, Chen et al. recently showed that the simple addition of nanoparticles is not sufficient to compatibilize the immiscible polymer phases in recycled HDPE/PET blends [144]. The authors proposed the simultaneous use of nanoparticles and chemical compatibilizers for improving mechanical properties and blend miscibility. Such a strategy was already pursued with encouraging results by Fang et al. for the production of a fully recycled polyolefin-based blend [145]. Similarly, Mural et al. optimized the mechanical performance of a blend of recycled PP and waste high impact polystyrene by adding both a copolymer and nanoparticles [146]. Stimulated by this new recycling perspective, Mnif and co-workers proposed to replace the conventional fillers for the manufacturing of automobile fenders with their nano-sized analogues, so as to facilitate the recycling of the final products by profiting from the presumed compatibilizing action of the nanoparticles [147,148]. On the other hand, it is important to mention the recent paper by Kazemi et al., who found that the uncontrolled presence of various kinds of nanoparticles in the waste plastics may also have a detrimental effect on the recycled products [149].

#### 3.3.2. Bio-plastics

Nanoparticles are effective compatibilizers even in case of biopolymers. In particular, interfacially-located clay particles were found to improve the interfacial adhesion between biodegradable polymers, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polylactic acid (PLA), thermoplastic starch (TPS) [150,151], as well as between bio-plastics and conventional petroleum-based polymers [152–154]. Among the various bio-plastics, PLA has received special attention because of its appreciable properties, which make it a promising candidate to replace petroleum-derived plastics. The main weaknesses of PLA are the brittleness and narrow temperature range of applicability, which is limited superiorly by the glass transition temperature ( $T_g < 60$  °C). Blending PLA with other bio-polymers in the presence of nanoparticles has proved to be effective for overcoming such limitations [42,155–157]. Among others, Nuzzo et al. ingeniously addressed the poor

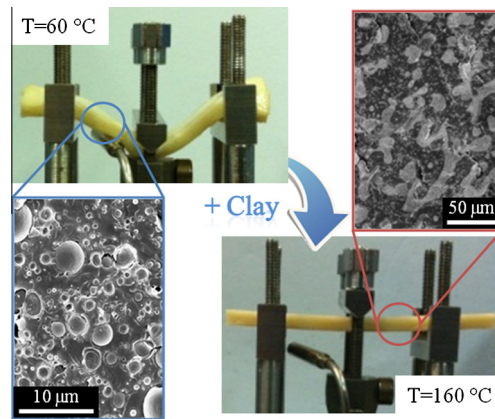


Fig. 12. Effect of small amounts of organo-clay on the morphology and creep resistance of a PLA/PA11 blend at 70 wt% of PLA. Readapted from [158].

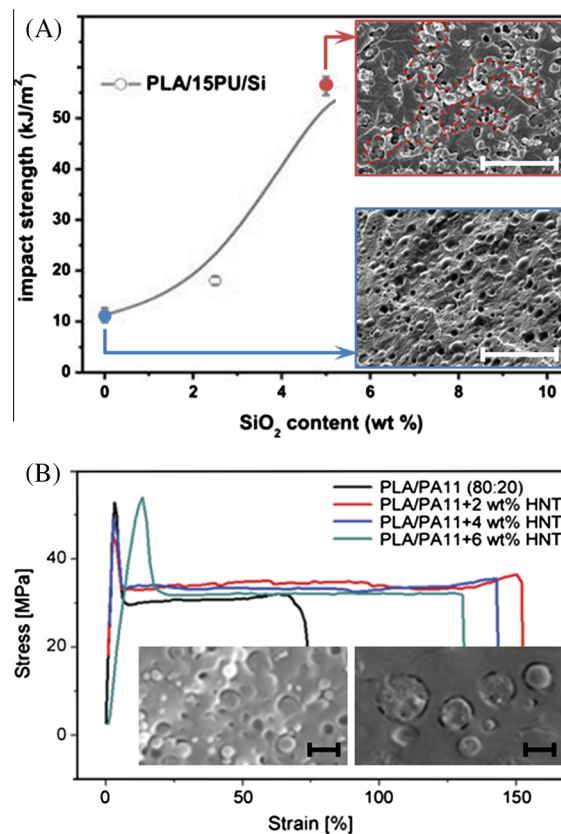


Fig. 13. Effect of nanoparticle-induced morphological transitions on the mechanical performances of PLA-based materials. (a) Impact strength as a function of the amount of silica nanoparticles in PLA/PU blends: the toughness increases due to the change from a sea-island to a network-like structure (Readapted from [78]). Scale bars = 5  $\mu\text{m}$ . (b) Tensile stress-strain curves showing the increased elongation at break of PLA/PA11 blends upon addition of HNT nanoparticles (readapted from [162]). Scale bars = 1  $\mu\text{m}$ .

mechanical performances of PLA at high temperatures by blending it with PA11, a bio-based and yet non-biodegradable semi-crystalline polymer with superior temperature resistance [158]. The goal was maximizing the content of the biodegradable PLA while preserving the continuity of the heat-resistant PA11. Clay nanoparticles were exploited to manipulate the blend microstructure. Specifically, the presence of organo-clay in the PA11 phase and interfacial region converted the drop-matrix morphology of the unfilled blend into a stable co-continuous one, in which the clay-rich PA11 phase forms a continuous framework that effectively contributes to bear stresses even well above the melting temperature of the major PLA phase (Fig. 12).

The authors also observed that maximizing the high-temperature creep resistance through nanoparticle addition may bring about an excessive material embrittlement at room temperature. Actually, the simultaneous reinforcing and toughening of PLA-based materials is as much desirable as challenging. An optimized balance between strength and toughness of PLA-based blends was obtained by tailoring the blend morphology by means of silica nanoparticles [78,159–161]. Different interpretations were proposed depending of the filler localization. In the presence of interfacially-adsorbed nano-silica, Yu and Huang correlated the simultaneous toughening and reinforcing of a blend of PLA and thermoplastic polyurethane to the improved interfacial adhesion between the polymer phases [160]. Differently, Xiu et al. ascribed the improvement in the impact toughness without detrimental effects on strength and modulus of a blend of PLA and poly(ether)urethane (PU) to the morphological transition from sea-island to network-like structure in the presence of nano-silica accumulated in the dispersed phase and in the interfacial region [78] (see Fig. 13a). Similarly, a noticeable toughening without sacrificing stiffness and strength was promoted by adding addition of halloysite nanotubes (HNT) to a PLA/PA11 blend [162]. In this case, besides improving the interfacial adhesion, the filler also promotes the formation of a salami-like structure, in which a HNTs-rich fibrillar PA11 phase actively contributes to the stress bearing (Fig. 13b).

Notable results were obtained also in case of plate-like nanoparticles. Among others, Ojijo et al. achieved a 29% enhancement of the elongation at break over that of neat PLA matrix upon addition of only 2 wt% of organo-clay to a blend of PLA and polybutylene succinate (PBS) [163]. Finally, an improvement of the elongation at break without losses in the tensile modulus was reported also by Chen et al. for a PLA/PBS system in the presence of a twice-functionalized organo-clay, which induced a considerable reduction of the size of the polymer drops [164].

#### 4. Final remarks

The intriguing perspective of imparting new physical properties and novel behaviors to a host polymer matrix through the simple addition of small amounts of nanoparticles is what really makes polymer nanocomposites attractive. Rather than aiming at the mere capitalization of the filler properties, the current trend is using nanoparticles as an active tool for manipulating the microstructure and, through it, the final performances of materials with phase-separated morphology, such as immiscible polymer blends. It has been shown that nano-sized fillers can (i) induce morphology refinement or coarsening, (ii) glue drops to form drop clusters, (iii) promote non-spherical polymer domains or (v) co-continuous microstructures, (v) stabilize the blend morphology in both quiescent and flow conditions. The ways in which nanoparticles affect the space arrangement of the polymer phase at micron-scale have been listed and carefully described. In particular, the recent literature has been rationalized by dividing the discussion in terms of typology of nanoparticles (spheres, plates and tubes) and preferential positioning of the filler (inside either of the bulk phases or at the polymer-polymer interface). Although the basic mechanisms remain often controversial, it has been possible to identify repeated patterns and general rules on which basing a focused selection of the materials to be used for obtaining nanocomposite blends with a desired set of properties. Selective reinforcement of specific material regions, simultaneous enhancement of mechanical strength and toughness, non-chemical compatibilization, low electrical percolation threshold, drastic improvement of the creep resistance, are some of the examples of the improvements potentially achievable through the judicious employ of nanoparticles. In our opinion, biopolymers and recycled plastics are among the materials that might readily benefit from such a simple and yet powerful strategy.

Finally, rather than using nanoparticles to manipulate the material morphology, we observe that many researchers are interested in the other side of the coin, viz. how to use immiscible liquids to drive the space arrangement of the nanoparticles, eventually realizing advanced nanostructures. Liquid-liquid interfaces of low-viscosity systems are already largely used as templates for guiding nanoparticle assembly [165]. The extension of such an approach to polymer systems is receiving growing attention in view of the possibility of slowing down the assembly processes by taking advantage from to the high viscosity of polymer melts [166,167].

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**Martina Salzano de Luna** received her PhD in Materials Engineering in 2015 at the University of Naples Federico II. As PhD candidate, in 2014 she was visiting student at the Imperial College London. Her doctoral research concerned the dynamic and structures of nanoparticles in polymer melts. She currently is a postdoctoral fellow at the Institute of Composite and Biomedical Materials of the National Research Council (Italy). Her current research interests include polymer nanocomposites and blends, bio-based polymers, and polymer nanocomposite coatings for conservation of cultural heritages.



**Giovanni Filippone** studied Materials Engineering at University of Naples Federico II, and he received his PhD in 2004 working on the rheology of elastomeric compounds for tire industry. In 2009 he obtained a permanent role as Assistant Professor, and since 2015 he is Associate Professor in Polymer Technology at the University of Naples Federico II. His main research interests concern the rheology, processing technologies, and structure-property relationships in polymer nanocomposites, polymer blends, and bio-based polymers.