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A Concept of Reactive Compatibilizer-Tracer for Studying Reactive Polymer Blending Processes

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Significance

A concept called reactive compatibilizer-tracer is proposed. The latter bears reactive groups capable of reacting with its counterpart on forming a copolymer for in situ compatibilization, and fluorescent labels allowing determining very small amounts of the in situ formed compatibilizer and formation of micelles when it occurs. Owing to this concept, it is shown that a reactive compatibilizer may be very efficient at the beginning of a reactive blending process and may suddenly become completely inefficient, resulting in an abrupt and drastic increase in size of the dispersed phase domains.
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Keywords: reactive blending, reactive compatibilizer-tracer, graft copolymer, polystyrene, polyamide 6

Introduction

Blending existing polymers can be a cost-effective way to develop new polymer materials. When a polymer pair is immiscible, which is the case for most polymer pairs, it is common practice to use a block or graft copolymer known as a compatibilizer to promote the dispersion of one of the phases in the another and stabilize the blend.[1–3] Such a compatibilizer can either be premade [4–10] or generated in situ during the blending process on reacting two reactive polymers at interfaces.[11–16] The latter case is called reactive polymer blending, in situ compatibilization or reactive compatibilization, and is mostly practiced in industries.

It is very challenging to investigate a reactive compatibilization process because both morphology development and interfacial reactions between reactive polymers are highly coupled. Most importantly, the amount of the in situ formed copolymer is often too low to be determined in a relatively accurate manner, especially for industrial processes. For this reason, we propose a new concept called *reactive compatibilizer-tracer*. It is an important extension of the concept of compatibilizer-tracer proposed previously.[17] A reactive compatibilizer-tracer bears reactive groups capable of reacting with its counterpart on forming a copolymer for in situ compatibilization of a reactive polymer blend, on the one hand, and fluorescent labels allowing determining very small amounts of the in situ formed compatibilizer, on the other hand.

This letter aims to show the concept of reactive compatibilizer-tracer with a concrete example. This concept is

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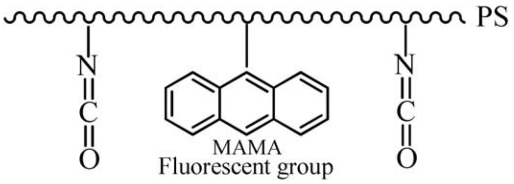
applied to reveal a phenomenon that a reactive compatibilizer may be very efficient at reducing the size of the dispersed phase domains at the initial stage of a reactive blending process, and may suddenly and completely lose its compatibilizing efficiency as the reactive blending process has proceeded to a certain extent. In other words, the dispersed phase is quickly reduced to small domains in size at the initial stage of the reactive blending process. At some point, these small domains suddenly and quickly grow in size, reaching a value similar to that without the reactive compatibilizer-tracer, instead of continuing to decrease or leveling off. This phenomenon indicates that a reactive compatibilizer which is very efficient under certain thermo-mechanical conditions may become inefficient under other ones. It also shows how challenging it may be to design and optimize the molecular architecture of a reactive compatibilizer as a function of thermo-mechanical conditions under which a reactive blending system is processed, a laboratory scale twin screw extruder vs. an industrial scale one, for example.

The concept of reactive compatibilizer-tracer is shown through polymer blends composed of polystyrene (PS) and polyamide 6 (PA6). The reactive compatibilizer-tracer is a polystyrene which bears certain numbers of isocyanate (3-isopropenyl-α, α-dimethylbenzeneisocyanate, TMI) and anthracene moieties (9-(methylaminomethyl)anthracene, MAMA) along its chain and in a random manner. It is denoted as PS-TMI-MAMA and is schematically shown below:



This reactive compatibilizer-tracer bears both common and specific features of reactive compatibilizers. First, its isocyanate (NCO) groups are chemically much more resistant to moisture than classical ones, and yet still have high reactivity toward the terminal amine of the PA6, forming a graft copolymer of PS and PA6 denoted as PS-g-PA6-MAMA. Second, the molar mass of the resulting graft copolymer can be determined by size exclusion chromatography (SEC) using a method developed previously.[18] Third and most importantly, the amount of the graft copolymer can be determined in an accurate manner using ultraviolet spectrophotoscopy (UV) owing to the anthracene moieties of this reactive compatibilizer. In fact, UV is able to quantitatively determine a few ppm of anthracene.[19] Forth, if the PS-g-PA6-MAMA graft copolymer forms micelles, they can be detected by confocal spectroscopy.

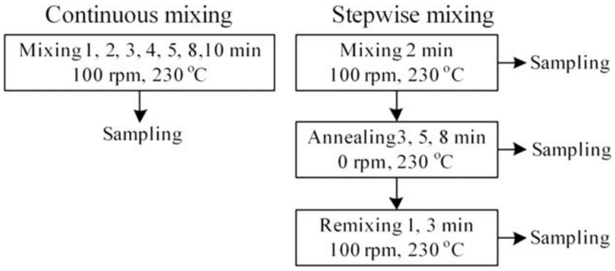
Experimental

Materials

The PS and PA6 used in this work were supplied by Yangzi-BASF, China, and UBE Nylon Ltd., Thailand, respectively. Their molar masses were measured by SEC using tetrahydrofuran (THF) as the eluent. The PA6 was *N*-trifluoroacetylated prior to the SEC measurement following the procedure described elsewhere.[18] Based on PS standards for the calibration, the number and mass-average molar masses of the PS were 101.3 and 228.8 kg/mol, respectively. Those of the PA6 were 19.4 and 49.4 kg/mol, respectively. Its terminal amine concentration measured by titration using aqueous hydrochloric acid was 0.0603 mol/kg. The reactive compatibilizer-tracer, PS-TMI-MAMA, was synthesized in the laboratory according to previous works.[17,20,21] Its number and average mass molar masses were 37.6 and 87.9 kg/mol, respectively. Its NCO content was 0.355 mol/kg, which amounted to 13.3 NCO groups per PS-TMI-MAMA chain on average.

Blending process

PS/PA6/PS-TMI-MAMA blends were processed in a batch mixer of type Brabender torque rheometer with a mixing chamber of 50 mL in capacity. The PS-TMI-MAMA content in the blends was always 1.5 wt % of the total mass of the PS and PA6. The mixing of the blending systems was ensured by the rotation of the two rotors of the mixing chamber. Two mixing modes were adopted, as show below:



One was continuous mixing, namely, 45 g of all the polymer components of a blending system were simultaneously charged to the preheated mixing chamber, and then mixed at 100 rpm and 230°C for various time intervals ranging from 1 to 10 min. The other mixing mode was stepwise mixing, namely, after the polymer components were charged to the mixing chamber altogether and mixed at 100 rpm and 230°C for a given time interval, the rotors stopped rotating, that is, 0 rpm or no mixing. The blending system was annealed under the quiescent condition at 230°C for a period of time and then the mixing was resumed at 100 rpm and 230°C. Once taken out of the mixing chamber at chosen time intervals, all samples were immediately quenched in liquid nitrogen to freeze-in their morphologies and interfacial reactions.

Determination of the amount of reacted PS-TMI-MAMA

The fluorescent labels of the PS-TMI-MAMA allowed determining the amount of the PS-TMI-MAMA that had reacted during the reactive blending process via SEC with a UV detector. MAMA had very strong UV-absorption at 367 nm while the PA6 and PS did not have any absorption there. Before the SEC measurement, the reacted PS-TMI-MAMA and the intact (nonreacted) one were separated from the blends in the following manner. About 1 g of the blend was introduced to a centrifuge tube filled with 50 mL (THF) at room temperature. The tube was then placed in a shaker to promote the dissolution of the PS and the intact PS-TMI-

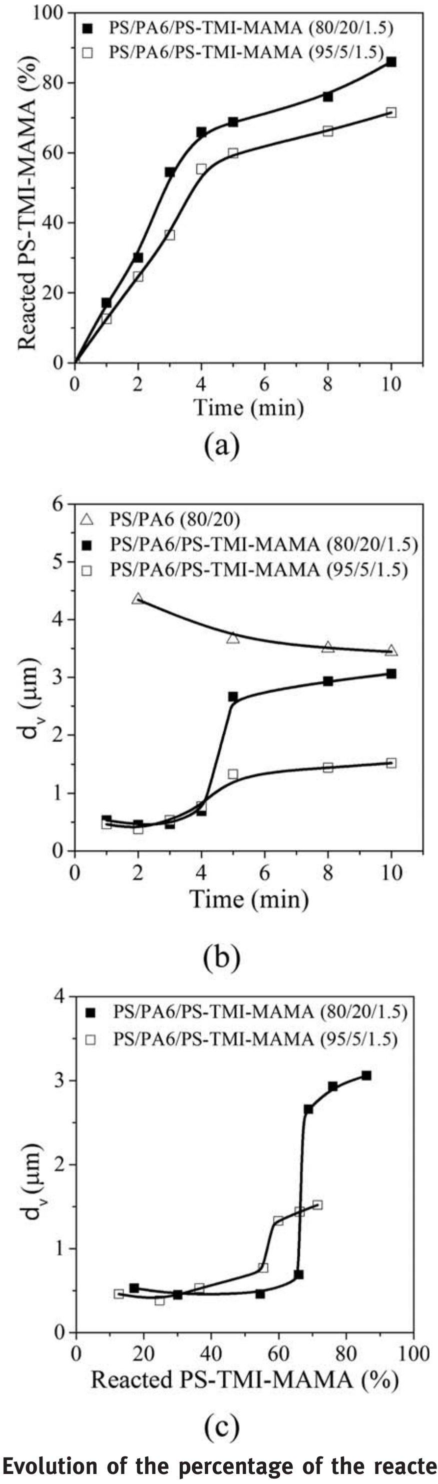


Figure 1. Evolution of the percentage of the reacted PS-TMI-MAMA (a) and that of the diameter of the dispersed phase domains (PA6) (b) of the PS/PA6/PS-TMI-MAMA reactive blends a function of mixing time for the continuous mixing case. The PS/PA6 (80/20) nonreactive blend in terms of d_v is shown as a reference. (c) Evolution of the diameter of the dispersed phase domains (PA6) of the PS/PA6/PS-TMI-MAMA reactive blends as a function of the percentage of the reacted PS-TMI-MAMA for the continuous mixing case.

MAMA. After 48 h of dissolution, the solution was centrifuged at 9000 rpm for 20 min. The supernatant solution was thrown away and THF was added to the tube. The solution in the tube was shaken for another 48 h. That process was repeated three times to thoroughly remove the PS and the intact PS-TMI-MAMA. The final insoluble products were mixtures of the nonreacted PA6 and PS-g-PA6-MAMA graft copolymer formed by the interfacial reaction between the PS-TMI-MAMA and PA6.

The PA6 and PS-g-PA6-MAMA became soluble in THF after they had reacted with *N*-trifluoroacetic anhydride (TFAA).[18] Before the *N*-trifluoroacetylation, the mixture of the PA6 and PS-g-PA6-MAMA was dried in a vacuum oven at 80°C for 12 h to remove moisture. About 0.03 g of the dried mixture was added to a flask followed by 4 mL CH_2Cl_2, 2 mL TFAA and 6 mL $CHCl_3$ in a sequential manner. After 24 h of reaction, the TFAA modified mixture was isolated by rotary evaporation at 30°C, and then dissolved in THF to prepare SEC solution with a concentration of 6 mg/mL. After the filtration, 50 μL of the solution was injected into a SEC apparatus of type Waters 1525/2414 equipped with a refractometer and a UV detector. Caution: the solution should be measured by SEC within a few hours after it was prepared. Otherwise, it would form gel.

Characterization of blend morphologies

The size of the PA6 domains in the PS matrix was characterized by scanning electron microscopy (SEM) of type ZEISS ULTRA55. Before the SEM observation, samples were fractured in liquid nitrogen, and immersed in formic acid at room temperature for 12 h to remove the dispersed phase domains (PA6) from the fractured surface, and finally dried in a vacuum oven at 80°C for 12 h. The dried samples were sputtered with gold and analyzed by SEM at 5 kV. A semiautomatic image analysis was used to determine the diameter of the dispersed phase domains. It was characterized by the volume average particle diameter, d_v, defined as follows

$$d_v = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \tag{1}$$

For each blend, at least 500 particles were counted for statistically meaningful values of d_v. In this work, the number average diameter followed the same trend as d_v.

The formation and size of PS-g-PA6-MAMA graft copolymer micelles in the PS/PA6 blends were examined by confocal microscopy. Polymer blends were cut to specimens of 1–2 mm thick and 1 × 1 cm^2 large. Fluorescent microscopy measurements were performed on an improved Leica Microsystems apparatus.[22] The fluorescence signal for anthracene was collected in the reflected light channel. All image acquisition procedures were performed at an excitation wavelength of 800 nm, with the pinhole fully opened (8.41 AU). A band-pass filter enabled to select the detection spectral range (400/25 nm center wavelength/bandwidth) for anthracene and to reject the infrared excitation beam.

Results

Figure 1 shows the evolution of the percentage of the PS-TMI-MAMA that has reacted with at least one PA6 chain and that of the diameter (d_v) of the PA6 dispersed phase domains of the PS/PA6/PS-TMI-MAMA blending system as a function of time under the continuous mixing conditions for two compositions: 95/5/1.5 and 80/20/1.5. As expected, the percentage of the reacted PS-TMI-MAMA first increases rapidly with increasing mixing time and then slows down with further increasing mixing time (Figure 1a). This is the case for both compositions. On the other hand, the diameter of the PA6 dispersed phase domains reaches about 0.5 μm in less than 1 min of mixing, and remains at this value for another 2 min of mixing (Figure 1b). It starts to drastically increase after about 4 min of mixing, reaching a value similar to the one without the reactive compatibilizer in less than 1 min.

Figure 1c shows the evolution of d_v as a function of the percentage of the reacted PS-TMI-MAMA. For both compositions, d_v starts to drastically increase when the percentage of the reacted PS-TMI-MAMA reaches a critical value of about 50% for the 95/5/1.5 and about 66% for the 80/20/1.5.

Figure 2 shows the evolution of the percentage of the reacted PS-TMI-MAMA and that of d_v of the dispersed phase domains (PA6) of the PS/PA6/PS-TMI-MAMA (80/20/1.5) reactive blending system as a function of time under the stepwise mixing conditions. The continuous mixing case and the PS/PA6 (80/20) nonreactive blend are shown as references. It is seen that when mixing stops after 2 min of mixing, the interfacial reaction almost stops too (Figure 2a). When it is resumed after 8 min of quiescent annealing, the interfacial reaction starts to proceed immediately again. This is in agreement with previous works.[16,23] Figure 2b shows that during the 8 min of quiescent annealing from 2 to 10 min, the dispersed phase domains have undergone little coarsening. When mixing is resumed, they suddenly increase in size and reach a value close to that of the PS/PA6 (80/20) without the reactive compatibilizer-tracer (PS-TMI-MAMA). This is very similar to the continuous mixing case.

Figure 2c compares the continuous and stepwise mixing cases for the PS/PA6/PS-TMI-MAMA (80/20/1.5) reactive blending system in terms of the evolution of d_v as a function of the percentage of the reacted PS-TMI-MAMA. Similar to the continuous mixing case, under the stepwise mixing the dispersed phase domains also suddenly increase in size when the amount of the in situ formed copolymer reaches a critical value of about 40%. However, this critical threshold is lower than that of the continuous mixing case which is 66%.

Discussion

The above experimental results show that the use of PS-TMI-MAMA as a reactive compatibilzer-tracer does allow determining very small amounts of in situ formed PS-g-PA6-MAMA graft copolymer during the blending process. Moreover, it has helped reveal a very interesting phenomenon that this reactive compatibilizer is very efficient at reducing the PA6 dispersed phase domain size at the beginning of the reactive blending process and that at a critical point it suddenly becomes completely inefficient, resulting in sudden and drastic morphology coarsening.

Generally speaking, this phenomenon is undesirable even catastrophic for reactive blending processes when it occurs. Nevertheless, one may also use it to advantage for synthesizing high purity copolymers. A question arises of why this

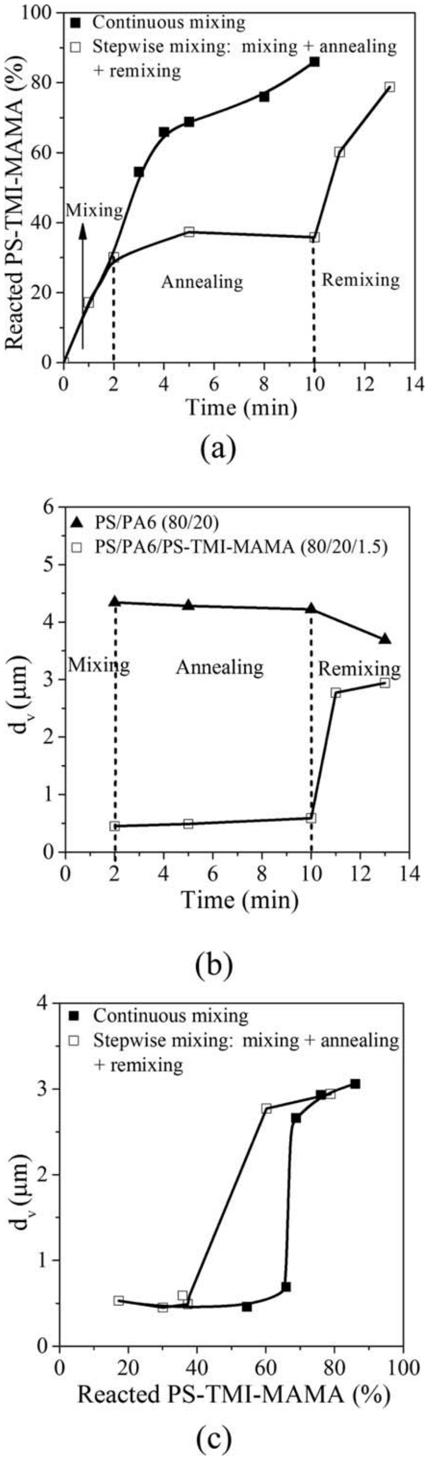


Figure 2. (a) Evolution of the percentage of the reacted PS-TMI-MAMA (a) and that of the diameter of the dispersed phase domains (b) of the PS/PA6/PS-TMI-MAMA (80/20/1.5) reactive blends as a function of time for the stepwise mixing case. The continuous mixing case and the PS/PA6 (80/20) nonreactive blend are shown as references. (c) Comparison between the continuous and stepwise mixing cases for the PS/PA6/PS-TMI-MAMA (80/20/1.5) reactive blend in terms of d_v as a function of the percentage of the reacted PS-TMI-MAMA.

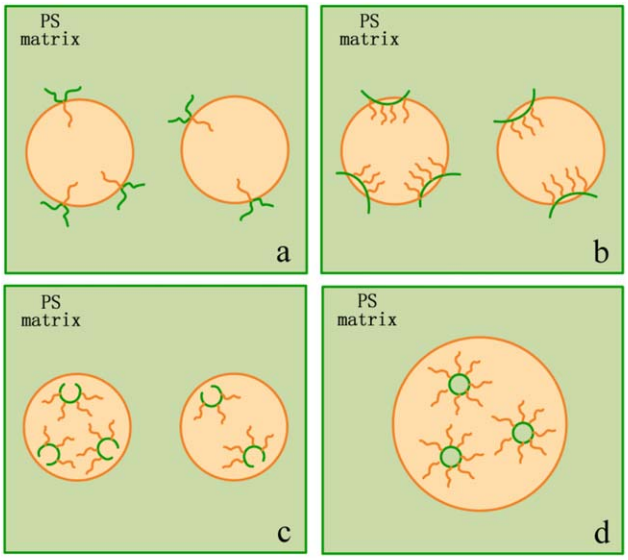


Figure 3. A sketch of the evolution of the molecular architecture of a copolymer formed by interfacial reaction, its pull-out from the interface and micelle formation.

(a) Y-shape copolymer, (b) comb-like copolymer, (c) pull-out of the copolymer from the interface (d) formation of micelles and coalescence of the dispersed phase domains due to the copolymer pull-out from the interface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phenomenon exists. What are the main parameters that influence it? How to control (suppress or promote) it? At the first glace, the above experimental results seem to suggest that the sudden and drastic increase in d_v is triggered by the formation of a critical amount of the PS-g-PA6-MAMA graft copolymer as a result of the interfacial reaction between the PS-TMI-MAMA and PA6. However, the underlying mechanism(s) responsible for this phenomenon may have nothing to do with the formation of a critical amount of the copolymer *per se*. An efficient compatibilizer has to have an appropriate molecular structure so that it stays at interfaces to reduce the interfacial tension.[24–35] An important feature of a typical reactive blending system such as the PS/PA6/PS-TMI-MAMA reactive blend is that both the amount and the molecular architecture of the in situ formed copolymer keep evolving during blending.

Thus, several scenarios of what may happen in the PS/PA6/PS-TMI-MAMA system could be envisioned. For example, Favis and coworkers proposed that once a sufficient amount of graft copolymer is formed, its high viscosity causes it to be eroded from the interfaces as a result of shear. The eroded copolymer would tend to form micelles.[36] The resulting PA6 dispersed phase domains would no longer have their compatibilized interfacial layers and they would coalesce in the usual fashion of a noncompatibilized system.

Another possible scenario is depicted in Figure 3. At the beginning of the reactive blending process, one PA6 chain is attached to the PS-TMI-MAMA (Figure 3a), forming a Y-shape copolymer at the interface. As the interfacial reaction proceeds further, more PA6 grafts may be attached to the PS-TMI-MAMA backbone and the resulting graft copolymer may become comb-like (Figure 3b). Once it is highly asymmetrical (for example, the number of PA6 grafts is high enough), it may become less attracted to the interface, and causing its detachment from interfaces (Figure 3c). These graft copolymer may form micelles in one of the polymer component phases and the dispersed phase would coalesce (Figure 3d). Mixing aggravates this detachment by literally pulling the copolymer off the interfaces.[37] Once the copolymer is no longer located at the interfaces, it losses completely its compatibilzing efficiency.

The above two mechanisms could operate in parallel and/or in synergy. They are corroborated by the results shown in Figure 2. Under the stepwise mixing, the dispersed phase domains also sharply increase in size when the amount of the in situ formed copolymer reaches a critical value of about 40%. This critical value is significantly lower than that of the continuous mixing case, namely, 66%. This indicates that quiescent annealing tends to decrease the threshold beyond which the catastrophic coarsening occurs. Why is there this difference? During the annealing, no mixing is applied. Therefore, no additional interfaces are generated and no fresh PS-TMI-MAMA chains react with the PA6 at the interfaces (Figure 2a). However, the PS-g-PA6-MAMA copolymer at the interface could continue to react with PA6, resulting in an increase in the number of PA6 grafts per PS chain as well as its viscosity. When the mixing is resumed, the PS-g-PA6-MAMA copolymer with a higher number of PA6 grafts could be more prone to detachment from the interface.

Let us consider the evolution of the interfacial coverage of the copolymer $\sum$ during reactive blending. $\sum$ is defined as the number of copolymer chain per interfacial area and can be estimated by Eq. 2

$$\sum = \frac{w_{\mathrm{cr}} N_{\mathrm{a}} \rho_{\mathrm{PA6}} d_v}{6\phi_{\mathrm{PA6}} M_n} \tag{2}$$

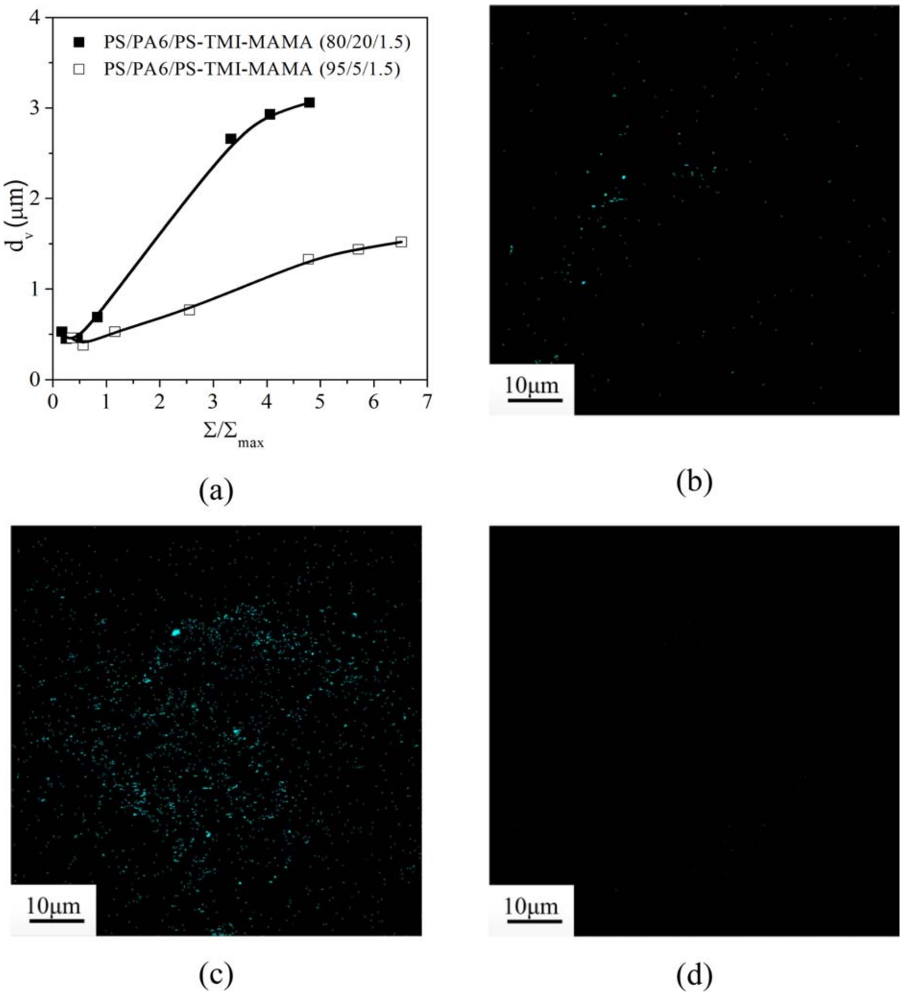
where w_{cr} is the percentage of reacted PS-TMI-MAMA, N_{a} is the Avogardro's number, ρ_{PA6} is the density of PA6 (1.14g/cm^3), d_v is the volume average dispersed phase domain size and M_n is the number average molecular weight of the compatibilizer. The maximum interfacial coverage, $\sum_{\mathrm{max}}$ can be estimated by assuming a dense monolayer of copolymers at the interface. Russell and coworkers came up with the following empirical equation for a block copolymer[38]

$$\sum\nolimits_{\mathrm{max}} = 2.06 N^{-0.39} \tag{3}$$

Kim et al.[39] found that a PS-g-PI graft copolymer has an interfacial area about 1.7 times that of a block analogue.

Figure 4a shows d_v as a function of $\sum/\sum_{\mathrm{max}}$ for the PS/PA6/PS-TMI-MAMA blend with two compositions. For the two compositions, d_v is very small when $\sum/\sum_{\mathrm{max}}$ is below 0.6. It tends to decrease with increasing $\sum/\sum_{\mathrm{max}}$ till the latter is about 0.6. Nevertheless this trend is not very clear, due to the narrow range of the data points. When $\sum/\sum_{\mathrm{max}}$ is above 0.6 or so, d_v starts to increase with increasing $\sum/\sum_{\mathrm{max}}$ and this trend continues even when $\sum/\sum_{\mathrm{max}}$ exceeds 1. This implies that the sudden and drastic increase in d_v shown in Figure 1b is not caused by an insufficient amount of the copolymer.

A value of $\sum/\sum_{\mathrm{max}}$ higher than 1 indicates that the amount of the copolymer is in excess compared with what is necessary to saturate the interfaces with a monolayer of the copolymer.



(a) (b)

(c) (d)

Figure 4. (a) Diameter of the dispersed phase domains as a function of the relative interfacial coverage of the copolymer $\sum/\sum_{max}$ for PS/PA6/PS-TMI-MAMA reactive blends. (b) and (c) Confocal fluorescent spectroscopy images of the PS/PA6/PS-TMI-MAMA (80/20/3) reactive blend after 2 and 10 min of continuous mixing, respectively. (d) Confocal spectroscopy image of the PS/PS-TMI-MAMA (80/3) control system after 10 min of continuous mixing. Turquoise dots correspond to the PS-g-PA6-MAMA graft copolymer micelles whose d_n and d_v are about 200 and 300 nm, respectively. These dots are better seen with eyes close to them enough.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The copolymer in excess is expected to form micelles. This is shown by the images of the confocal spectroscopy of the PS/PA6/PS-TMI-MAMA (80/20/3) blend after 2 min (Figure 4b) and 10 min of continuous mixing (Figure 4c). It is seen that there are much more micelles (corresponding to turquoise dots) in the blend with 10 min of mixing than in the one with 2 min of mixing. This supports the above statement that the detachment of the in situ formed PS-g-PA6-MAMA graft copolymer from the interfaces is responsible for the loss of its compatibilizing efficiency. The d_n and d_v of the micelles seen by the confocal microscope are 200 and 300 nm, respectively. The minimum size of micelles seen by the confocal microscope is 150 nm.

The above discussion suggests that the number of reactive groups a reactive compatibilizer bears should not be too high. Otherwise, the molecular architecture of resulting graft copolymer could be highly asymmetrical so that it would be prone to detachment from the interfaces, especially under mixing.

Conclusion

This article has proposed a concept of reactive compatibilizer-tracer. It has allowed showing, for the first time, that a reactive compatibilizer may be very efficient in the initial stage of the reactive blending process and may suddenly and completely lose its compatibilizing efficiency at a certain point, resulting in an abrupt and drastic increase in the size of the dispersed phase domains which quickly reaches a value close to the corresponding nonreactive system. Detachment of the in situ formed graft copolymer from the interfaces is responsible for the sudden deterioration of its compatibilizing efficiency. It is aggravated by static annealing and/or mixing.

Acknowledgments

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