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**Citation for published version (APA):**

Bharatia, A., Hejmady, P., Cardinaels, R., Seo, J. W., & Moldenaers, P. (2017). Inducing conductivity in immiscible PS/PP blends by a percolated polyaniline/PA filler selectively localised by specific interactions. In A. Maazouz (Ed.), *Proceedings of PPS 2016: The 32nd International Conference of the Polymer Processing Society - Conference Papers* [050002] (AIP Conference Proceedings; Vol. 1914). American Institute of Physics. <https://doi.org/10.1063/1.5016719>

**DOI:**

[10.1063/1.5016719](https://doi.org/10.1063/1.5016719)

**Document status and date:**

Published: 14/12/2017

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Citation: [AIP Conference Proceedings](#) **1914**, 050002 (2017); doi: 10.1063/1.5016719

View online: <https://doi.org/10.1063/1.5016719>

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# Inducing Conductivity in Immiscible PS/PP Blends by a Percolated Polyaniline/PA Filler Selectively Localised by Specific Interactions

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**Abstract.** We describe an approach to develop conducting immiscible blends of polystyrene (PS) and polypropylene (PP) with a percolated polyaniline/polyamide (PANI/PA) filler in the presence of a SEBS-g-MA compatibilizer. The underlying principle of the work is the ability of the compatibilizer to concurrently stabilize the bi-phasic morphology to develop co-continuous blends and to improve the dispersion of the filler by specific interactions. From the latter perspective, we have chosen a percolated composite of PANI in PA as the filler and prepared its master batches with the compatibilizer expecting that specific interactions between the amino end groups of PA and the MA anhydride groups in SEBS-g-MA would result in a better dispersion of PANI. The effect of master batch preparation method using either melt mixing or solution casting on the conductivity was studied, and the latter technique was found to be superior. As a result, the concomitant effect of morphology stabilization with improved PANI dispersion led to an improved connectivity of PANI in the phase of the blend where it selectively localizes (PS) for 40/60 PS/PP blends. To further improve the connectivity of PANI, we studied the effect of different sequence additions of the solution casted master batch to the blend components. Melt mixing the solution casted master batch with PS followed by PP resulted in double percolated PANI selectively localized in the continuous PS phase owing to their specific interaction in 50/50 PS/PP blend. This resulted in an increase of the dc conductivity by 6 decades in comparison to the neat blend, already at low PANI concentrations (6 wt%). The connectivity of the blend was affirmed by the power law behavior of the viscoelastic response, more in particular the storage modulus  $G'$ , of the percolated blends. Furthermore, the effect of the compatibilized blend morphology on the dc conductivity and viscoelastic response was investigated by varying the blend composition. In summary, the proper choices of using a master batch preparation technique by solution casting and subsequently melt mixing the master batch with the polar PS phase followed by PP led to the formation of a double percolated network of filler in the continuous PS phase at low PANI concentrations.

**Keywords:** Immiscible blends, Compatibilization, Electrical percolation, Morphology, Specific interactions

**PACS:** 83.80.Tc; 83.60.Bc; 72.80.Le; 47.57.Ng; 83.85.Vb; 72.80.Le; 72.80.Tm

## INTRODUCTION

Following the rising demand of flexible conducting polymeric materials in EMI shielding, electronic industries and robotics, immiscible polymeric blends with conducting nanoparticles have generated tremendous interest. This popularity stems from the ability to tune the electrical properties of immiscible blends by tailoring their morphology combined with selective nanoparticle localization, thereby facilitating the formation of a percolated particle network. Another class of conducting materials that finds widespread use in batteries, display devices and sensors are intrinsically electrically conducting polymers, which combine the chemical and mechanical properties of polymers with the electronic properties of metals.<sup>1</sup> However, immiscible blends with electrically conducting polymers have far

less been investigated. This is due to the fact that conducting polymers have limited thermal stability and difficult processability, and therefore it seems a good alternative to use them as fillers in polymer blends similar to the use of conducting particles.<sup>1</sup>

In our work, we have developed conducting immiscible PS/PP blends containing a conducting polymer (PANI) in order to retain the electrical properties of PANI at a low concentration in the polymer blend. The approach adopted was to employ a SEBS-g-MA compatibilizer to concurrently generate and stabilize a co-continuous morphology and to improve the dispersion of PANI by specific interactions. To achieve the latter, we have chosen a percolated composite of PANI in PA as the filler and have prepared its master batches by melt mixing or solution casting with the compatibilizer. Our conjecture of an improved dispersion of the filler is based on possible reactive compatibilization of the amino end groups of PA and the anhydride group of –MA.<sup>2</sup> Furthermore, a study of the effect of sequence addition of the suitable master batch to the blend components was used to tune the connectivity of the filler based on the specific interactions between the filler and the blend components. Thus, we have exemplified a novel method for tailoring a percolated network of a conducting polymer in an immiscible blend.

## EXPERIMENTS

Master batches (MB) of compatibilizer (SEBS-g-MA) (20 wt%) and filler (F) (80 wt%), the latter being a percolated composite of PANI (30 wt%) in PA were prepared by either melt mixing or solution casting. Melt mixing of the MB was performed at 150 °C and 60 rpm for 3 min under inert nitrogen with simultaneous addition of the components. The processing temperature was below the melting point of the filler and PANI was thermally stable during the mixing. To prepare the MB by solution casting, toluene was used, which is a non-solvent for PANI/PA whereas SEBS-g-MA dissolves readily in toluene. A mixture of SEBS-g-MA and PANI/PA in toluene was first stirred for 1 hr at room temperature (RT) and subsequently bath sonicated for 1 hr at RT, after which drying at 80 °C for 8 hr resulted in solution casted films of the MB.

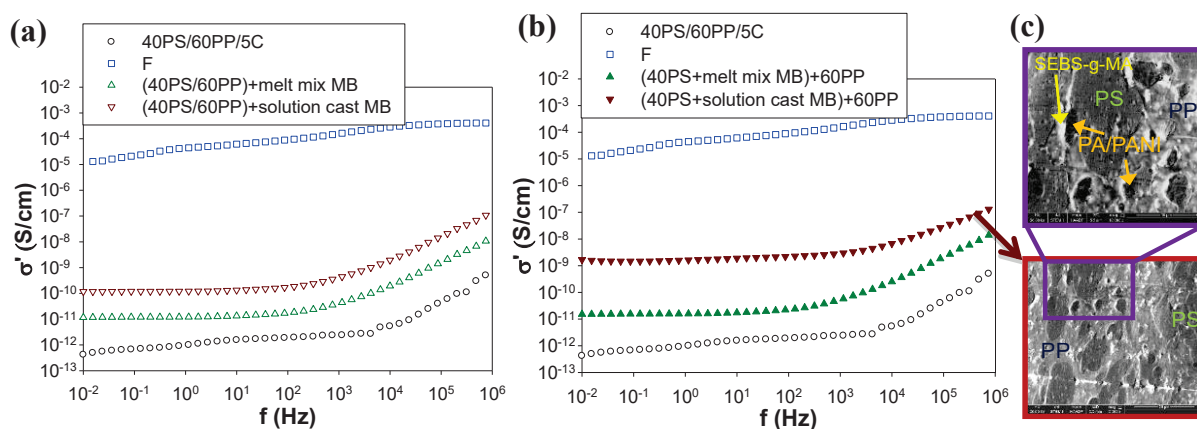
As the state of dispersion and specific localization of the filler are contingent on the specific interactions of the filler with the compatibilizer and the blend components, we systematically performed various sequence additions of both types of master batches to the blend components. All subsequent melt mixing was performed at 150 °C and 60 rpm. The viscosity ratio of the PS/PP blend at 150 °C was 0.16. In the first sequence, 40/60 (wt%/wt%) PS/PP blends were melt mixed for 3 min, after which MB (5 wt%) was added and further allowed to mix with the immiscible blend for 3 min. For the second sequence, PS (40wt%) and MB were melt mixed for 3 min and afterwards PP (60 wt%) was added to the blend and mixing proceeded for 3 min. As the polar PS phase has more favorable interactions with the MB as compared to PP, the study aimed to develop a percolation of PANI in the PS phase,<sup>3</sup> due to which the possible sequence of mixing the MB with PP was not pursued. In addition to the 40/60 PS/PP blends, blends with the solution casted master batch were prepared for various blend compositions in which the PS content was varied between 30 and 70 wt%. All prepared samples were compression molded at 150 °C before characterization of the blend conductivity, linear viscoelastic moduli and morphology.

## RESULTS AND DISCUSSION

### Effect of Sequence Addition: Melt Mixing versus Solution Casted Master Batches

In this section, a comparison of the conductivity exhibited by 40/60 PS/PP blends containing master batches prepared by either melt mixing or solution casting is presented. The MB has been added to the blend in different sequences, which allows choosing the most optimal master batch preparation technique as well as sequencing addition. The conductivity spectra of the neat compatibilized blend, the PANI/PA filler (F) and the blends prepared by adding various MB to a premixed PS/PP blend are shown in Figure 1a. The neat blend has a nearly insulating character owing to the non-conducting components. Upon addition of the melt mixed MB to the blend, an increase by a decade of the frequency independent conductivity (dc conductivity) is attained, which further increases by one more decade for the blend with solution casted MB. The low frequency conductivity is a signature of the connectivity of the filler. As the dc conductivity of the blend is significantly lower than that of the filler, the dispersion and/or distribution of the MB within the blend is clearly far from optimal, thus suggesting the need for a different sequence addition. The conductivity spectra of blends in which different MB were first premixed with PS followed by addition of PP are shown in Figure 1b and are compared with that of the neat blend and the filler. Upon addition of the solution casted MB, the dc conductivity is about 2 decades higher as compared to that of blends

containing the melt mixed MB. This could be corroborated by the presence of elongated and partially connected PS domains laden with filler, as shown in the STEM micrograph of Figure 1c. From Figure 1, it is imperative to emphasize the near insulating character of the blends with the melt mixed MB and the fact that the blend conductivity remains unaffected upon changing the blending sequence. In addition, the dc conductivity of the blend with solution casted MB is consistently higher than that of blends with the melt mixed MB. Also, for blends with solution casted MB, the second sequence (Figure 1b) results in a slightly improved conductivity as compared to the first sequence (Figure 1a). The latter can be attributed to an improved state of dispersion of the filler owing to van der Waals interactions between the phenyl group of PS and the PANI.<sup>3</sup> In summary, blends with solution casted MB exhibit an enhanced dc conductivity as compared to blends with the melt mixed MB and the addition sequence of the MB facilitating its specific interaction with the blend component PS further yields an improvement in the conductivity. We have thus used solution casted master batches for subsequent blend preparation and the effect of the sequence addition of the MB will be investigated further.



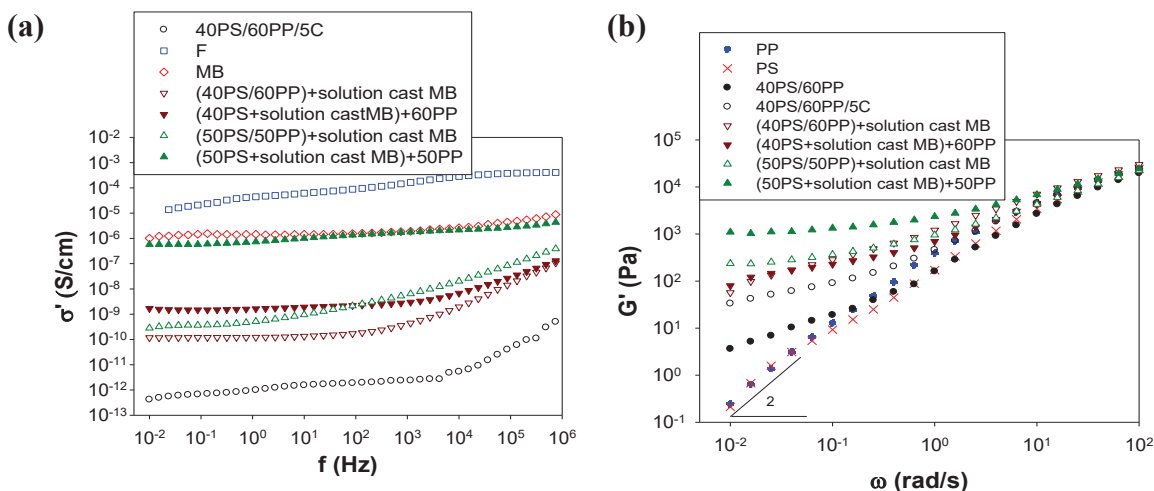
**FIGURE 1.** Comparison of conductivity spectra of neat blend with compatibilizer (C), filler (F) and blends with different sequence additions (a, b) of melt mixed and solution casted master batches (MB). (c) STEM image of blend with solution mixed MB using the sequence of (b).

## Effect of Sequence Addition for Solution Casted Master Batch: Consequence of Blend Composition

To further elucidate the effect of the sequence addition of the MB to the blend constituents, the study has been extended to blends with equal composition (50/50 PS/PP blend) to possibly augment the relative changes in the dc conductivity. Hence, the conductivity spectra for blends prepared with various sequences of solution casted master batches have been shown in Figure 2a for 40/60 and 50/50 PS/PP blends, in which PS is the continuous phase in the former and PP in the latter (from STEM image). Upon comparing the conductivity of the various blends with that of the neat blend and the MB, it is apparent that the sequence of adding the MB to PS followed by addition of PP is optimal for both the blend compositions. In addition, it is imperative to emphasize that the difference in dc conductivity between the different sequences is significantly higher for 50/50 blends (over 3 decades) as compared to that of 40/60 blends (one decade) prepared under identical conditions. The former also exhibits a frequency independent conductivity identical to the dc conductivity of the solution casted MB. This is a manifestation of an electrical percolation of PANI with an effective concentration of 6 wt% (20 wt% filler containing 30 wt% PANI in PA) owing to the formation of a double percolated network of the filler in the continuous PS phase. The blend morphology will be subsequently studied by the storage modulus  $G'$  of the blends. In summary, a percolation of PANI at 6 wt% in an immiscible PS/PP blend was achieved with suitable choice of master batch preparation technique and the addition sequence of the MB to the blend components.

To gain further insight in the morphology of the blends whose conductivity is provided in Figure 2a, the viscoelastic response of the blends is shown in Figure 2b. The blend components display a typical terminal behavior at low frequencies ( $G' \approx \omega^2$ ). For 40/60 blends prepared with different addition sequences, a pronounced elastic contribution in  $G'$  is observed in comparison to neat blend primarily owing to the increased interface upon compatibilization. However, there is no remarkable effect of the sequence addition on the elastic response. This is in agreement with the mitigated effect of the sequence addition on the conductivity owing to the presence of

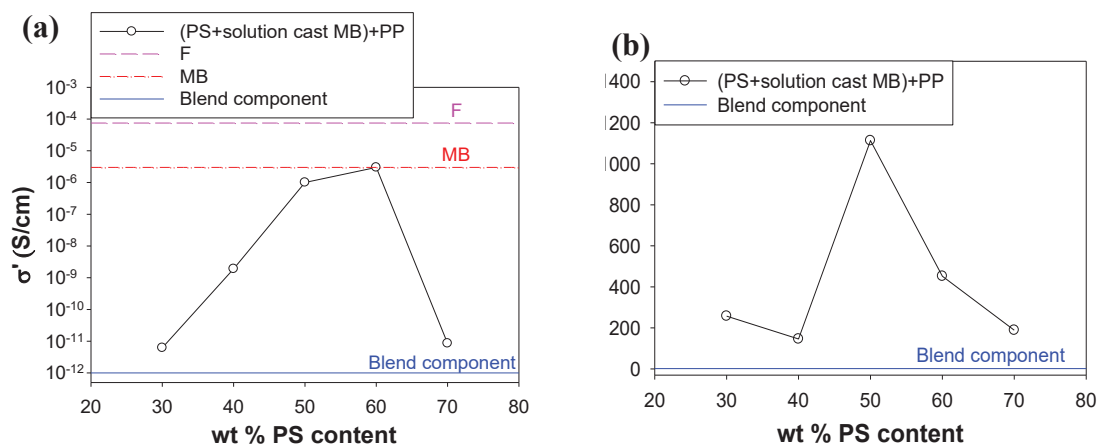
disconnected PS domains laden with the filler. On accessing the viscoelastic response ( $G'$ ) of the 50/50 blend with MB prepared by addition to the premixed PS/PP blend, a power law behavior is displayed with  $G' \approx \omega^{0.32}$ . This weak frequency dependence of  $G'$  is indicative of connectivity of the blend components. Conversely, the MB does not percolate in Figure 2a in the continuous PS phase. This could be attributed to a lack of specific interactions of the MB and the blend components, which might lead to agglomeration of the filler. Our argument can further be verified by studying the viscoelastic response of the 50/50 blend exhibiting electrical percolation (Figure 2a) in which a nearly frequency independent response of  $G'$  is observed ( $G' \approx \omega^{0.17}$ ) for blends with solution casted MB extruded first with PS followed by addition of PP. This is ascribed to the occurrence of PP and PS domains with different length scales and thus disparate relaxation times, characteristic of a co-continuous morphology of the blend.<sup>4</sup> In summary, a continuity of the phase in which the filler specifically localizes (PS) combined with an improved dispersion of the filler owing to its favorable interactions with PS and the compatibilizer unequivocally led to a double percolated network of the filler in Figure 2a. Hence, the sequence of melt mixing solution casted MB and PS followed by mixing with PP will be subsequently investigated for other blend compositions.



**FIGURE 2.** Comparison of (a) conductivity spectra and (b) linear viscoelastic response (storage moduli  $G'$ ) for 40/60 and 50/50 PS/PP blends with different sequence additions of solution casted master batches (MB). For comparison in (a) the conductivity spectra of the neat blend, filler and the MB are shown and in (b)  $G'$  of the blend components is provided.

### Effect of Blend Composition: Blends with Solution Caster Master Batch and Optimal Sequence Addition

In order to obtain the optimal blend properties, it is highly interesting to investigate the effect of blend composition, resulting in different morphologies on the connectivity of the filler for blends with solution casted MB melt mixed with PS followed by addition of PP. Hence, the dc conductivity obtained from the conductivity spectra of blends for various compositions (% PS) is shown in Figure 3a and compared with the dc conductivity of the filler (F), MB and blend components. As expected blends with nearly equal compositions exhibit a pronounced increase in the conductivity owing to the double percolation of the filler in the continuous PS phase. To probe the connectivity of the filler, the low frequency storage moduli (at 0.02 rad/s) for various compositions (% PS) are shown in Figure 3b. A pronounced increase in the  $G'$  of 50/50 blends is due to formation of a bi-continuous network of the filler in the continuous PS phase. The fact that the 60/40 blend exhibits electrical percolation in Figure 3a and an attenuated  $G'$  in Figure 3b suggests that we are not probing the percolated network of the filler but the co-continuous morphology of the blend. In addition, an increase in  $G'$  for the 30 wt% PS blend could possibly be ascribed to the presence of elongated and perhaps connected domains of PS, as 20 wt% filler selectively localizes in the PS. Hence, a one to one correspondence of dc conductivity and elastic response is not obtained as we are probing the percolated PANI network in 50/50 blends and the blend morphology in 60/40 blends. In summary, we have developed conducting blends by formation of double percolated networks of PANI (6 wt%) for several blend morphologies with solution casted MB melt mixed first with the blend component having specific interactions.



**FIGURE 3.** Comparison of (a) dc conductivity and (b) linear viscoelastic response (storage modulus  $G'$ ) at 0.02 rad/s for blends with varying PS/PP concentrations with filler (F) and solution casted master batch (MB) (a) and blend component (a and b).

## CONCLUSION

In our study, we have successfully demonstrated how master batch preparation techniques consisting of melt mixing or solution casting can be used to tune the dispersion of a conducting polymer, percolated PANI in PA. This was achieved by interactions of the amino end groups of the PA of the filler and the MA anhydride group of the compatibilizer. Furthermore, the sequence of addition of the solution casted master batch to the PS phase helped to specifically localize the filler in the PS phase due to their specific interactions. In summary, the compatibilizer concurrently led to a stable continuous network of the PS phase with an improved PANI dispersion, thereby facilitating the formation of a double percolated network of PANI in the continuous PS phase. As a result a synergistic increase in the conductivity of the percolated blend by 6 decades as compared to that of the neat blend was achieved. The connectivity of the blend was further verified by the power law behavior of the dynamic viscoelastic moduli. Using suitable choices of solution casted master batch and the sequence addition of the master batch to the PS phase, we investigated the effect of various compatibilized blend morphologies on the connectivity and the viscoelastic properties of the blends in order to reduce the effective percolation threshold of PANI in the blend. In conclusion, a suitable choice of master batch preparation technique combined with the addition of the master batch to the blend component having specific interactions can be used to tune a percolated network of a conducting polymer at low concentrations for blends with various morphologies. To further elucidate the contributions of the specific interactions between the MA anhydride group of the SEBS-g-MA and the amino groups of PA, FTIR and TGA analysis of the MB as well as study of blends with SEBS as a non-functionalized compatibilizer or pure PANI as a non-reactive filler will be performed.

## ACKNOWLEDGMENTS

This research has been partially funded by GOA/09/002. Ruth Cardinaels is indebted to the Research Foundation Flanders (FWO) for a Post-doctoral Fellowship at KU Leuven.

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