

Elastomer particle morphology in ternary blends of maleated and non-maleated ethylene-based elastomers with polyamides: Role of elastomer phase miscibility

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Abstract

The elastomer particle morphology in ternary blends of maleated and non-maleated ethylene-based elastomers with polyamides has been examined. The elastomers used include an ethylene/propylene copolymer, EPR, with a maleic anhydride (MA) grafted version, EPR-*g*-MA, and an ethylene/1-octene copolymer, EOR, with maleated versions EOR-*g*-MA-*X*% where *X* is 0.35, 1.6 or 2.5. The polyamides used were nylon 6 and an amorphous polyamide, Zytel 330 from DuPont. The morphology development was explored from both thermodynamic and kinetic points of view where the former refers to miscibility of the elastomers and the latter might include the ratio of the elastomers, the matrix type, the order of mixing, mixing intensity, i.e. the extruder type, and graft structure, etc. Both sources influence the morphology developed. For ternary blends with EPR-*g*-MA/EPR, the morphology (particle size and distribution) seems to be well controlled via the level of maleation in the rubber phase. The two polyamides generate comparable rubber particle sizes at the same of MA level. For ternary blends with EOR-*g*-MA/EOR, the morphology strongly depends on the level of MA; the rubber particle size, in general, is much smaller in nylon 6 blends than in Zytel 330 blends. Morphology of ternary blends with EOR-*g*-MA/EOR is much more complex than that of blends with EPR-*g*-MA/EPR due to the co-existence of miscibility limits and the kinetic factors. Miscibility of maleated EOR elastomers is examined via transmission electron microscopy (TEM) using a special staining technique; a miscibility boundary, as revealed by TEM, occurs around $\Delta(\%MA) = 0.9 - 1.25$ MA%. If the two elastomers are miscible, a unimodal particle size distribution always appears in blends regardless of the kinetic factors; however, if immiscibility prevails, either a unimodal or bimodal particle size distribution may develop depending on the ratio of the elastomers and the matrix type. The order of mixing and the mixing intensity do not seem to change the modality of the size distribution.

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1. Introduction

Toughening of semi-crystalline polyamides, like nylon 6 and 66, by blending with functionalized elastomers has been extensively reported [1–17]. Extensive efforts have been made to tailor the morphology of the dispersed elastomer phase, and it is well established that particle size and its distribution play a crucial role in governing the level of toughening [10,16,18]. Of course, other issues like the elastomer type and content are important as well. The focus of recent work [16,19,20] has been on the mechanistic reasons for why there are minimum

and maximum elastomer particle sizes for generating super-tough blends.

An early proposal by Wu [4] suggested that the key parameter is interparticle distance rather than particle size per se. The majority of the literature [6,7,21–25] interprets the scale effects in terms of cavitation of the rubber phase and the subsequent triggering of shear yielding of the matrix due to relief of the state of triaxial tension ahead of the advancing crack. Another point of view is that rubber particles can alter the crystalline structure of the matrix in ways that facilitate toughening [15,26]. Recent work by Leibler et al. has addressed this issue through experiments that alter the crystalline organization of the matrix [27]. Certainly a better understanding of how the matrix morphology and characteristics affect toughening and other performance parameters is needed.

Our strategy has been a more extreme one in which we seek to compare the toughening responses and mechanisms of

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a purely amorphous polyamide (Zytel 330 from Du Pont) with that of the more well-investigated semi-crystalline polyamides like nylon 6, nylon 66, etc. In a prior paper [28], we demonstrated the toughening of this amorphous polyamide using combinations of a styrene-triblock copolymer having a hydrogenated mid-block, SEBS, with a maleic anhydride functionalized version, SEBS-*g*-MA, of this elastomer. In many ways the toughening behavior of this amorphous polyamide was rather similar to that of the semi-crystalline polyamides. In that work, it was possible to demonstrate that there is an upper limit on rubber particle size for effective toughening just as in the case of the crystalline polyamides. However, unlike the case of nylon 6, we were not able to generate small enough rubber particles to establish any lower size limit for this amorphous polyamide. This difficulty stems in part from the end-group configuration of this amorphous polyamide which makes it difficult to make the needed small particles. A maleated rubber capable of forming a wider range of rubber particle sizes including both the upper and the lower limit would be desirable for making this comparison of the toughening of amorphous versus crystalline polyamides. In addition, we were interested in exploring how the nature of the elastomer phase affects the toughening response of the two classes of polyamides.

Thus, we have extended our previous work to include maleic anhydride functionalized ethylene-propylene (EPR) and ethylene-1-octene (EOR) random copolymers for toughening. Our commercial sources of maleated EPR did not identify materials with grafting levels higher than 1.14 wt% MA. However, we were able to acquire a series of EOR elastomers with maleic anhydride grafting levels up to 2.5 wt%. These higher grafting levels provide more possibilities of generating smaller particle sizes. Interestingly, only a few reports have appeared on toughening polyamides using such maleated EOR elastomers [29,30].

The morphology (particle size and its distribution) of the dispersed phase may be controlled via the level of maleation in the rubber phase by using a mixture of maleated and non-maleated elastomers in varying proportions in the formulation. Such use of a combination of maleated and non-maleated elastomers has been reported to be a simple but effective way for tailoring rubber particle size [10,14,17], although doing so may potentially incur immiscibility between the two elastomer components due to the increased polarity caused by maleation. That is, two maleated rubbers with different levels of MA may not necessarily be miscible depending on the difference in MA level and their molecular weights. Such immiscibility, if it exists, complicates the morphology development during reactive blending with polyamides and may lead to bimodality in rubber particle distribution as has been reported in ternary blends of nylon 6 with maleated and non-maleated polypropylene [31]. Thus, it is useful to know if these maleated elastomers with different levels of MA are miscible with each other or not. In addition to the thermodynamics effects (miscibility), many kinetic or non-equilibrium factors influence the morphology of a blend; some of these factors might include: the ratio of two elastomers, the matrix type, the order

of mixing, mixing intensity, i.e. the extruder type, and graft structure, etc. Obviously, the co-existence of both thermodynamic and kinetic factors makes the morphology development even more complicated. The morphology, undoubtedly, determines the final mechanical properties including Izod impact strength of the blend.

The broader purpose of this work is to explore and compare in some detail the toughening effect between a semi-crystalline (nylon 6) and an amorphous polyamide matrix (Zytel 330) using combinations of EPR with a maleated version, EPR-*g*-MA, and, combinations of EOR with maleated versions, EOR-*g*-MA-*X*%. This paper reports the effects of miscibility, as revealed by transmission electron microscopy (TEM), between maleated EOR elastomers with different levels of MA, i.e. EOR-*g*-MA-*X*% versus EOR-*g*-MA-*Y*% ($X \neq Y$), on the nature of the rubber particle size distribution in blends with both polyamides. In addition, the effects of kinetic factors including the ratio of two elastomers, the matrix type, the order of mixing and mixing intensity, i.e. the effect of extruder type on the morphology development of blends will be presented. A subsequent paper [32] will report rubber toughening effects of these two types of rubbers when nylon 6 and Zytel 330 are the matrix polymers. The effects of rubber content, rubber particle size and its distribution associated with these thermodynamic and kinetic factors on Izod impact strength and the ductile–brittle transition temperature will be considered. A final paper [33] will explore the fracture behavior of selected blends in more detailed ways.

2. Experimental section

Table 1 summarizes pertinent information about the materials used in this study. The structure of the amorphous polyamide [28,34] has been described previously. The EPR and EPR-*g*-MA have been used in prior work from this laboratory for toughening semi-crystalline polyamides [10,17]. The ethylene-1-octene copolymer, designated as EOR, is the precursor material for maleated versions [35], designated as EOR-*g*-MA-*X*%, where *X* is 0, 0.35, 1.6 or 2.5. Prior to melt compounding, all materials containing nylon 6 and a-PA were pre-dried for at least 16 h in a vacuum oven at 80 °C while the elastomers were dried for at least 16 h in a convection oven at 65 °C. Most blends containing nylon 6 and all blends containing a-PA were prepared using a Haake co-rotating, intermeshing twin screw extruder ($D=3.05$ cm, $L/D=10$) operated at 240 °C and 280 rpm; the configuration of mixing elements in this extruder was described previously [28]. Selected blends containing nylon 6 were prepared using a Killion single screw extruder ($D=2.54$ cm, $L/D=30$) having an intensive mixing head operated at 240 °C and 40 rpm. Binary blends of the EOR elastomers (without polyamides), used for examination of miscibility, were made in the single screw extruder at the same processing conditions.

The effect of the order of mixing of the three components on blend morphology was explored using three different sequences of adding the various components. Most of the blends were made by vigorously mixing all components

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