



# Enhancement in interfacial reactive compatibilization by chain mobility



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## ABSTRACT

This study investigates the role of polymer chain mobility, through the addition of a plasticizer, N-butylbenzene sulfonamide (BBSA), on the overall blending dynamics and interfacial copolymer chain formation in the reactive blending of brominated poly(isobutylene-co-*p*-methylstyrene) (BIMSM) and polyamide (PA). Compared to a non-reactive poly(isobutylene-co-*p*-methylstyrene) (IMSM)/PA blend, the reactive BIMSM/PA blend demonstrates a rapid, order of magnitude increase in viscosity, and attains a plateau viscosity at higher temperatures. The addition of a BBSA plasticizer (5–10 wt%) surprisingly increases the viscosity even further, suggesting an enhancement in interfacial reaction due to increased chain mobility. It is also found to increase the level of grafting from about 46 to 57% and has a significant influence on the morphology of the blend system. It is shown that the reactive grafting has an onset at lower temperatures for the blend system with 10 and 43% plasticizer. The morphologies of the blends with 5–10% plasticizer have a more uniform distribution ( $d_v/d_n$ ) with a reduced  $d_v$  for the dispersed BIMSM particles. At 43 wt% plasticizer the blends show an increased phase size resulting from the significantly enhanced phase coalescence. These results indicate that enhanced chain mobility through plasticizer usage can impact interfacial compatibilization and phase coalescence and that a threshold level of 5–10 wt% plasticizer provides an optimum level of chain mobility for this reactive blending system.

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## 1. Introduction

In heterophase polymer blends, the interfacial tension is the predominant thermodynamic driving force for phase separation between blend components. In interfacially compatibilized blends, either in situ generated or pre-made compatibilizers are used to achieve a certain degree of compatibility between blend components. Both the dispersion and interfacial adhesion improve in these interfacially compatibilized blends [1].

In situ reactive protocols are often preferred due to their overall ease, cost, and performance. Both theoretical [2–5] and experimental studies have examined different aspects of reactive polymer blending, including: the effect of the molecular weight of the

reactants [6], the influence of a particular reaction protocol [7–8], the inter-diffusion of the reactive species [9], the location of the reactive group on the backbone [9], as well as the kinetics or rate of the reaction [10] on the interface, blend morphology, interfacial tension, and coalescence. Reactions in the bulk and at the interface in heterogeneous systems have also been evaluated [11–12]. It was found that some reactions are diffusion controlled while others are reaction rate controlled [12]. In general, the rate of the reaction in heterogeneous systems is found to be higher than that in homogeneous systems [9]. A number of studies have investigated the effect of interfacial copolymer molecular architecture, its composition, molecular weight, chain length, and the concentration on the morphology. [13–14]

In previous work, the morphology in reactively processed brominated poly(isobutylene-co-*p*-methylstyrene) (BIMSM) and polyamide (PA) blends has been studied [15–16]. Pendant bromine moieties in BIMSM react with terminal amines from PA by a nucleophilic substitution reaction to form a BIMSM-PA graft

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copolymer with a comb-type architecture. We found this interfacial reaction to be aggressive producing as much as 46 wt% graft copolymer in about 3 min of mixing time. Based on this and various other fundamental observations an ‘interfacial erosion’ mechanism was proposed for morphology development in this blend system [15]. The mechanism considers the formation of a very high viscosity graft copolymer right at the interface during dynamic mixing. The viscosity mismatch between the formed graft copolymer and the other constituents of the blend leads to the subsequent erosion of interphase material to form fine, nanometer-sized micelles. The removal of the copolymer from the interface exposes non-reacted material and primes the interfacial region for further copolymer formation. In this fashion, most of the BIMSM reacts resulting in a blend comprising a nanoscale dispersion with a number-average diameter of 50–80 nm and a volume average diameter of 300 nm. In another work [16], it was found that the reaction and PA plasticization shift elastomer percolation thresholds and continuity development to higher concentrations. Furthermore, it was shown that the level of plasticizer significantly influences the extent of reaction as shown in Fig. 1.

It is well known that plasticizers permeate in between polymer chains leading to increases in the intermolecular distance and free volume and to reductions in the secondary bonding forces between polymer chains [17]. In addition, the plasticizer reduces polymer chain entanglements and interchain friction. It suppresses the glass transition temperature, hence, the “plasticizer” name, and improves the flexibility, ductility, toughness, and ultimately, the processability [17]. Hodge et al. [18] studied the effect of water as a plasticizer on the free volume, chain mobility, and glass transition behavior of poly(vinyl alcohol) (PVOH) by spectroscopic and dynamic mechanical analysis. They attributed the effective plasticization to strongly bound water to the hydroxyl groups of PVOH. It raised free volume, enhanced lubrication, and swelled polymer chains resulting in a disruption of polymer–polymer hydrogen bonding and a corresponding decrease in the glass transition temperature. Several authors [19–21] have noted similar effects of increase in polymer chain mobility with the addition of the plasticizer in many different systems.

Antiplasticization occurs in glassy polymers when an additive having strong interactions with a given polymer leads to a decrease in the free volume. This results in an increase in the glass transition temperature as well as a significant increase in the stiffness and

brittleness of the material. The phenomenon depends inversely on the molecular weight of the additive and may diminish at higher additive concentrations where it may act as a plasticizer [22–23]. Gaudin et al. [24] for a starch–sorbitol–water system observed that at low sorbitol content (<27%), the chain mobility in fact decreases due to antiplasticization while above that level (>27%) the sorbitol becomes a plasticizer enhancing the mobility of the system. Anti-plasticization effects can be found in a variety of systems [22–25]. In semi-crystalline polymers, antiplasticization may occur as a result of enhanced crystallization. The increased polymer chain mobility facilitates the formation of the crystalline segments, which results in a decrease in the free volume, with the addition of a plasticizer.

Despite the scientific and technological importance of plasticizers in polymer processing, very few studies have examined the role of plasticizers on chain mobility in the reactive blending of multiphase systems. The objective of this work is to examine the influence of plasticizer-enhanced chain mobility on the rheological and morphological dynamics of an in-situ reacted system.

## 2. Experimental procedures

### 2.1. Materials

In this study, IMSM (poly(isobutylene-co-*p*-methylstyrene)) and BIMSM (brominated poly(isobutylene-co-*p*-methylstyrene)) elastomers from ExxonMobil Chemical and a random copolymer of PA 6 ( $\approx 85$  wt%) and PA 6,6 ( $\approx 15$  wt%) from Ube Chemical were used. *N*-Butylbenzene sulfonamide (BBSA) was used as a plasticizer for PA. The molecular weights, composition, other material specific characteristics and shear rate are summarized in Table 1. The shear rate values of individual materials were estimated under actual melt blending conditions of 205 °C and 100 rpm in a Brabender internal mixer equipped with roller type rotors [26].

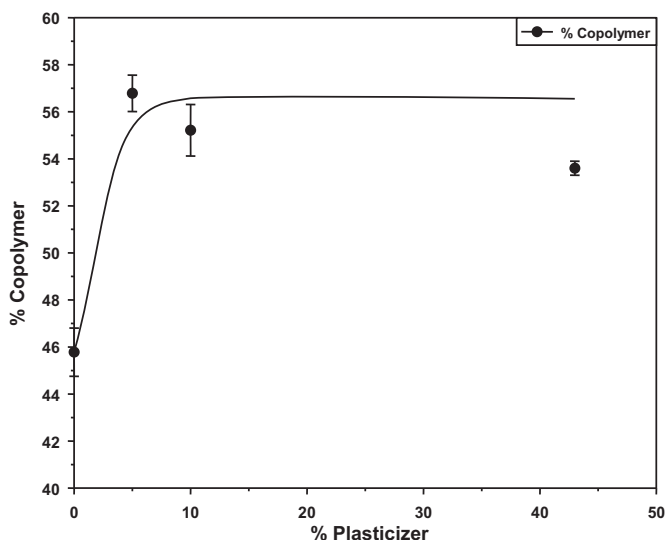
### 2.2. Rheological characterization

The basic rheological behavior of the pure materials was characterized using a Bohlin constant stress rheometer (CSM) in a dynamic mode. The experiments were performed using a parallel plate geometry of 25 mm diameter and under a nitrogen atmosphere. The frequency sweep tests were conducted at a constant shear stress of 100 Pa and with multiple samples within the time window permitted by a time sweep test. The results shown are an average of at least three measurements. More details of the technique used can be found elsewhere [15–16].

Advanced rheological measurements were performed using an Anton Paar Physica MCR 501 rheometer installed with 50 mm parallel plate geometry and CTD 401 type heating chamber. These temperature-dependent rheological measurements were conducted to study the effect of chain mobility on the extent of the interfacial grafting reaction between BIMSM and PA. They were performed under constant steady shear (CSS), i.e. under constant rotational speed to keep the shear rate constant, and using a temperature ramp of 1 °C/min.

**Table 1**  
Materials properties.

#	Material	Supplier	Bromine content (mole %)	$M_n$	$M_w$	Shear rate ( $s^{-1}$ )
1	IMSM	ExxonMobil	0	226 K	530 K	16
2	BIMSM	ExxonMobil	0.75	184 K	450 K	16
3	PA 6/6,6	Ube	0	30 K	36 K	89



**Fig. 1.** Effect of plasticizer on the amount of graft copolymer produced [16].

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