

# Continuity development in polymer blends of very low interfacial tension

Prashant A. Bhadane<sup>a</sup>, Michel F. Champagne<sup>b</sup>, Michel A. Huneault<sup>b</sup>,  
Florin Tofan<sup>c</sup>, Basil D. Favis<sup>a,\*</sup>

<sup>a</sup> CREPEC, Department of Chemical Engineering, École Polytechnique de Montréal, 2900 Édouard Montpetit, P.O. Box 6079, Station Centre-Ville, Montréal, Qué., Canada H3C 3A7

<sup>b</sup> Industrial Materials Institute, National Research Council of Canada, 75 de Mortagne Blvd., Boucherville, Qué., Canada J4B 6Y4

<sup>c</sup> Lavergne Group, 8800 Crescent 1, Ville d'Anjou (Montréal), Qué., Canada H1J 1C8

Received 15 November 2005; accepted 17 January 2006

Available online 3 March 2006

## Abstract

Phase continuity development and co-continuous morphologies are highly influenced by the nature of the interface in immiscible polymer blends. Blends of ethylene–propylene–diene terpolymer (EPDM) and polypropylene (PP) possess an interfacial tension of about 0.3 mN/m and provide an interesting model system to study the detailed morphology development in a very low interfacial tension binary system. A variety of blends with viscosity ratios of 0.2–5.0 and shear stresses of 11.7–231.4 kPa were considered. Using a variety of sophisticated morphology protocols it is shown that at low blend compositions, the dispersed phase actually exists as stable fibers of extremely small diameter of 50–200 nm and the continuity develops by fiber–fiber coalescence. An analysis using break-up times from Tomotika theory also supports the notion of highly stable dispersed fiber formation. These results challenge the current view of the dispersed phase as small spherical droplets. It is shown, under these conditions, that a seven-fold variation in the viscosity ratio has virtually no influence on % continuity or morphology, while a large change in the matrix shear stress from 11.7 to 90.9 kPa has an important effect on pore diameter. Both sides of the continuity diagram are studied and highly symmetrical continuity behavior is observed with composition. In fact a single master continuity curve is observed for these blends varying in viscosity ratio from 0.7–5.0 and with shear stresses from 11.7–90.9 kPa. Although the glass transition temperatures indicate that these materials are completely immiscible after melt mixing and cooling, it is shown that the blends demonstrate the morphological features of a partially miscible system. These results support a concept that the blend was partially miscible during melt blending, at which time the gross morphological features of the blend were developed, but becomes fully phase separated upon cooling. It appears that the quenching of the EPDM/PP blend from the melt is rapid enough to preserve the imprint of that partial miscibility on the gross blend morphology.

© 2006 Elsevier Ltd. All rights reserved.

**Keywords:** Polymer blends; Co-continuous morphology

## 1. Introduction

Today, polypropylene (PP) is produced on a massive scale because of its versatile properties and for years now, the unfavorable low temperature brittleness of PP has been overcome by blending it with different elastomers. Ethylene–propylene–diene terpolymer (EPDM) has been found to be the most successful elastomer in blending with PP due to: the very low interfacial tension ( $\sigma$ ) ( $\approx 0.3$  mN/m at 190 °C) [1–6] and the low glass transition temperature of EPDM ( $\approx -40$  to  $-50$  °C) [7–12]. Furthermore, the EPDM can be crosslinked,

which opens up numerous advantages as a thermoplastic vulcanizate (TPVs) [13–16].

At low compositions in PP and when the viscosity ratio is near unity, the EPDM phase has been reported to form very fine dispersed spherical domains. Number average particle sizes as low as 0.2  $\mu\text{m}$  have been reported in the literature for blends prepared via melt mixing [17–22] making this one of the finest blend morphologies reported in the polymer blend literature.

Many authors have reported EPDM/PP blends to be immiscible [7,19,23–28], however, the miscibility–immiscibility issue in this blend system is very complex and controversial. In the past, Lohse et al. [26], by small angle neutron scattering (SANS) and more recently Han et al. [28] by determining the solubility parameter through pressure–volume–temperature ( $P$ – $V$ – $T$ ) properties measurement, demonstrated that unlike atactic-PP (aPP), EPDM is immiscible both in the melt and on cooling from the melt with isotactic-PP (iPP).

\* Corresponding author. Tel.: +1 514 340 4711x4527; fax: +1 514 340 4159.

E-mail address: [basil.favis@polymtl.ca](mailto:basil.favis@polymtl.ca) (B.D. Favis).

This is the case even when the ethylene content of the elastomer is as low as ca. 8%. However, recent similar SANS experiments carried out by Seki et al. [29] with deuterated-EPDM (unlike Lohse who used deuterated-PP) prepared with metallocene catalyst indicated that these blends are a homogeneous one-phase mixture in the melt.

Chen et al. [8] found EPDM/PP blends to be immiscible below an upper critical solution temperature (UCST) determined by the crystallization temperature curve and above a lower critical solution temperature (LCST) from cloud point measurements. Thus, these blends are miscible in the temperature range in between the UCST and LCST. Inaba et al. [30,31] have reported that immiscible EPDM/PP blends phase separate by a spinodal decomposition mechanism above their melting temperature. The crystallization takes place and proceeds in and through PP-rich domains without invoking the long-range rearrangement of PP molecules. These discussions demonstrate the complexity and controversial nature of the miscibility–immiscibility issue in EPDM/PP blends.

Recently, Marin et al. [32] studied the co-continuous morphology development in partially miscible poly(methyl methacrylate) (PMMA)/polycarbonate (PC) blends. Both polymers are amorphous in nature and possess an interfacial tension of 0.6 mN/m. In that work it was shown that, because of the partial miscibility, the blend demonstrated significantly different morphological features as compared to that reported for fully immiscible blends of low interfacial tension by Li et al. [33]. Marin et al. found that these partially miscible blends exhibited very fine dispersed phase morphologies, artificially high percolation thresholds, and attained co-continuity at higher than expected compositions of the minor phase. Furthermore, these blends demonstrated significant coalescence effects as a function of dispersed phase composition as compared to the highly stable morphologies observed for fully immiscible binary blends of low interfacial tension. Marin et al. carried out a detailed correction of the phase composition and continuity phenomena by treating the blend as a mixture of PMMA-rich and PC-rich phases. Once these corrections were carried out, the continuity phenomena in terms of percolation onset and attainment of co-continuity fell in line with the expected behavior for a low interfacial tension binary system.

Despite their commercial significance, detailed morphological studies of EPDM/PP blends are lacking in the literature. In particular, continuity development and co-continuity are virtually untreated for this blend system. Furthermore, this system provides an excellent view into the blend morphology development of systems with very low interfacial tension. This paper is the first of a series of works that will examine the morphology development in EPDM/PP blends in a highly detailed fashion. Future works will involve examination of continuity development and co-continuity in high viscosity ratio blends and the relationship of the final crosslinked morphology to the initial non-crosslinked morphological states.

## 2. Experimental procedures

### 2.1. Materials

Three EPDM elastomers with different Mooney viscosities and two different types of PP homopolymers with significantly different melt flow indexes were used in this study. The materials do not contain any fillers. The ethylene and diene content of all the grades of EPDM were kept as similar as possible to eliminate any effect of these variables on the study. All EPDM grades contain ethylidene norbornene (ENB) as the diene. A small amount (0.5 wt%) of Irganox B 225 antioxidant was added to the mixture to reduce the oxidative degradation of PP. Further details concerning the materials are given in Table 1.

### 2.2. Rheological characterization

The neat EPDM, and PP containing 0.5 wt% Irganox B 225 were compression molded at 190 °C in the form of disks for rheological characterization. The rheological characterization was carried out using a Bohlin constant stress rheometer (CSM) in the dynamic mode. The experiments were performed using a parallel plate geometry of 25 mm diameter, at 190 °C and under a nitrogen atmosphere. An oscillation mode at 0.1 Hz frequency was used to test the stability of the materials at the test temperature. Both PP homopolymers, after addition of an antioxidant, were found to be stable, however, all the grades of EPDM showed the tendency to crosslink (as indicated by the increase in viscosity over time). Thus, several samples were used to carry out rheological experiments, so as not to exceed the time window revealed by the time sweep test. A stress sweep was then performed from 0.3 to 2420 Pa to determine the region of linear viscoelasticity. The frequency sweep tests were performed in an experimental window permitted by the time and stress sweep tests.

### 2.3. Melt blending

PP, EPDM, and antioxidant were first dry blended in a beaker and the mixture was fed all together into the mixing chamber. The two polymers were melt blended using a Haake Rheomix 600 internal mixer equipped with a 69 cm<sup>3</sup> chamber and roller-type rotors for 8 min at 100 rpm and at 190 °C. Under these mixing conditions an average shear rate of 27 s<sup>-1</sup>

Table 1  
Characteristic properties of the materials

Polymer	Supplier	Given name	Molecular weights × 10 <sup>3</sup>		Ethylene content (%)	ENB content (%)
			<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>		
PP	Basell	PP 1	89	288	–	–
PP	Basell	PP 2	166	773	–	–
EPDM	Bayer	EP 1	71.2	141.9	62	4.0
EPDM	Bayer	EP 2	112.4	194	52	4.3
EPDM	Bayer	EP 3	146	241.1	53	4.3

Download English Version:

<https://daneshyari.com/en/article/5190817>

Download Persian Version:

<https://daneshyari.com/article/5190817>

[Daneshyari.com](https://daneshyari.com)