

# Manipulating the Morphology of Poly(ethylene terephthalate) Blends by Capillary Rheometry

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## INTRODUCTION

The versatile nature of polymer blends has made them an object of research for many years. One of the application fields of polymer blends is food packaging where poly(ethylene terephthalate) (PET) blends with improved barrier properties have been of great importance. Poly(m-xylene adipamide) (MXD6) or poly(ethylene-co-vinyl alcohol) (EVOH) have been used as the supporting polymers in high gas barrier applications. In polymer blending systems, morphology control which is closely related to the rheological properties of the blend components is of prime importance since the final properties including barrier properties of polymer blends will depend, to a large extent, on the morphology of the dispersed phase, such as its size and shape [1]. In most studies [2-7, 8-16], blends prepared with different blend ratios have been deformed by using a rotational rheometer without damaging the microstructure and the resulting morphological changes have been correlated with the rheological properties of the blend components and the flow conditions. The purpose of this study is to reveal the possible co-continuous phase structure created by the minor component during real processing conditions. Capillary rheometer was chosen intentionally since rheological data obtained with its usage simulate the real processing conditions. In this regard, this study is the first work on the generation of a co-continuous microstructure by using the rheological data delivered by capillary rheometer for PET blends.

## EXPERIMENTAL

**Materials.** Matrix polymers and compatibilizer were provided by Artenius UK in the form of extruded pellets. Matrix polymer is Melinar B60® (CSD Grade PET, IV:0.82 dL/g, Artenius UK). Disperse phases are poly(m-xylene adipamide) (Nylon-MXD6 Grade 6007, Mitsubishi Gas Chemical Company, Inc.) with a molecular weight of 25,000 g/mole and EVAL™ SP-434 (EVOH with 32 mole % ethylene content, EVAL Europe N.V.). A PET copolymer consisting of 5 wt.% sodium sulfonated isophthalate (PET-co-5SIPA, Artenius UK) was used as the compatibilizer for PET/MXD6 blends. The amount of PET-co-5SIPA was 10 phr for PET/MXD6 blends. Polymers were dried before use. The drying conditions for both rheological measurements and extrusion process were as follows: PET at 175°C for 6 hours, MXD6 and EVOH at 85°C for 14 hours in an air-circulating oven. Drying of PET-co-5SIPA was carried out at 175°C for 14 hours in vacuo.

**Blend Preparation.** Preparation of PET/MXD6 and PET/EVOH blends with and without the compatibilizer was performed by using a co-rotating intermeshing twin screw extruder (Leistritz Micro 27 LG 44D, Ø = 27 mm) with a length to diameter ratio of L/D: 44. The screw profile is made up of conveying and kneading elements, also using opposite pitch to ensure melting, mixing, shearing, and a good dispersion of the components. A processing temperature of 270°C was chosen according to the rheological measurements. The extrusion process was carried out with a screw rotation speed of 100 rpm (throughput: 4.5 kg/h) and 200 rpm (throughput: 9 kg/h). The extrudates were cooled in water and pelletized.

## CHARACTERIZATION

**Rheology Analysis.** Melt shear viscosity measurements of the neat materials were carried out at constant shear rate test by using a Rosand RH-10 twinbore high pressure capillary rheometer. Testing temperatures were 260°C, 265°C, 270°C, 275°C, and 280°C. The range of shear rate was 100-5000 s<sup>-1</sup>. Polymers were dried before measurements as mentioned above.

**The Rheological Model.** Viscosity data were collected versus shear rate with the help of capillary rheometer and these data were used for co-continuity predictions at shear rates present during extrusion. Such estimates of the compositional location of the co-continuous region in extruded blends are commonly made from viscosity data using a variety of relationships. The most common empirical relationship used to describe co-continuity is the Jordhamo equation:[8]

$$\frac{\eta_A}{\eta_B} \cong \frac{\varphi_A}{\varphi_B}$$

In this equation,  $\eta$  represents the viscosity (Pa.s) and  $\varphi$  the volume fraction of the components of the binary blend. On the basis of the viscosity data, it is possible to calculate the point of phase inversion, i.e. co-continuity for the non-compatibilized blends and to compare it with the experimental results.

**Morphology Analysis.** A Leo G34-Supra 35VP scanning electron microscope (SEM) was used for studying the microstructure of the blends. To that end, the samples were cryogenically fractured and coated with the help of a carbon evaporator prior to SEM analysis.

## RESULTS

In order to be able to simulate the real processing conditions, a common parameter in extruders and rheometers should be found. Shear rate applied during processing in extruders and generated during working on capillary rheometers is the common parameter which is employed for determination of the phase co-continuity. Mohamed et al. [17] and Wu [18] have shown that the average shear rate generated in twin screw extruder varies between 53 and 100 s<sup>-1</sup> depending upon screw speed. Assuming that the shear rate generated in the extruder is 100 s<sup>-1</sup>, the related calculations were made by using the rheological data obtained with this shear rate value. The shear viscosity values at 100 s<sup>-1</sup> are tabulated for PET and MXD6 in Table 1, and for extruded PET and MXD6 at 270°C in Table 2. Volume fractions necessary for the observation of co-continuity point are also shown in the related tables by employing the Jordhamo equation.

Table 1. Shear Viscosity and Volume Fraction Values for PET/MXD6 Blends at Different Temperatures

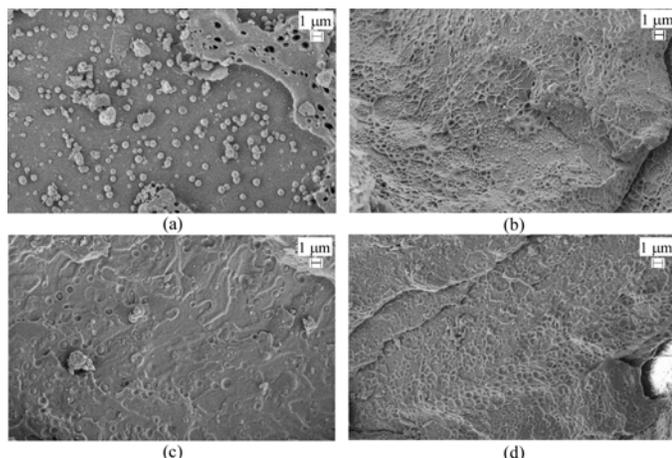
Temperature (°C)	Shear Viscosity at 100/s (Pa.s)		Viscosity Ratio	Volume Fraction (vol.%)	
	PET	MXD6	PET/MXD6	PET	MXD6
260	1121	120	9.34	90.33	9.67
265	532	75	7.09	87.64	12.36
<b>270</b>	483	40	12.08	<b>92.35</b>	<b>7.65</b>
275	492	42	11.71	92.13	7.87
280	324	32	10.13	91.01	8.99

Table 2. Shear Viscosity and Volume Fraction Values for PET/MXD6 Blends Calculated From Shear Viscosity Values of the Materials Extruded at Different Screw Speeds (Processing Temperature: 270°C)

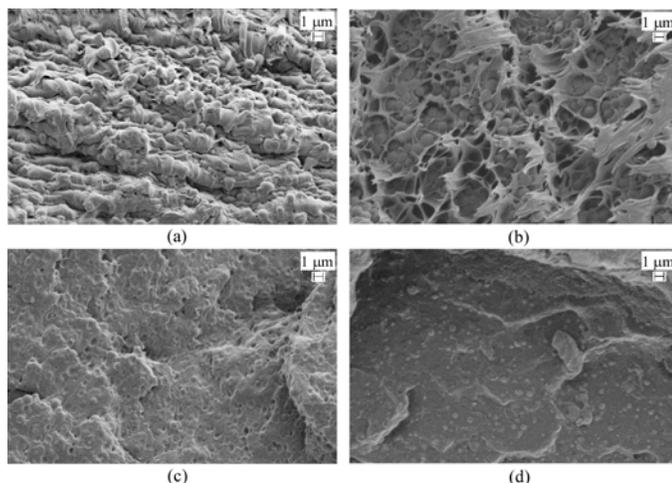
Screw Speed	Shear Viscosity at 100/s (Pa.s)		Viscosity Ratio	Volume Fraction (vol. %)	
	PET	MXD6	PET/MXD6	PET	MXD6
100	219.33	70	3.13	75.8	24.2
200	207.99	38	5.47	84.5	15.5

According to the morphological investigations, the PET/MXD6 blends (92.35/7.65 (v/v), 84.5/14.5 (v/v) with/without containing the compatibilizer, 75.8/24.2 (v/v) with the compatibilizer) show a dispersed phase distribution with a spherical shape instead of a co-continuous morphology. On the other hand, the blend containing 24.2 vol.% MXD6 without employing PET-co-5SIPA has a quasi-interpenetrating structure together with rod-like and unclear

droplet/matrix structure which disappears with the addition of PET-co-5SIPA. Addition of the compatibilizer deteriorates the desired microstructure obviously. As a result, Jordhamo relationship is valid for uncompatibilized blends.



**Figure 2.** SEM micrographs of the extruded PET/MXD6 (92.35/7.65 v/v) blends with/without using a compatibilizer, Abbreviations: (a). PET/MXD6 (screw speed: 100 rpm, throughput: 4.5 kg/h), (b). PET/MXD6 with 10 phr PET-co-5SIPA as compatibilizer (screw speed: 100 rpm, throughput: 4.5 kg/h), (c). PET/MXD6 (screw speed: 200 rpm, throughput: 9 kg/h), (d). PET/MXD6 with 10 phr PET-co-5SIPA as compatibilizer (screw speed: 200 rpm, throughput: 9 kg/h). The volume fractions of PET and MXD6 were calculated according to the shear viscosity values of the virgin materials (magnification x10000).



**Figure 3.** SEM micrographs of the extruded PET/MXD6 blends with/without using a compatibilizer, Abbreviations: (a). PET/MXD6 (75.8/24.2 v/v) (screw speed: 100 rpm, throughput: 4.5 kg/h), (b). PET/MXD6 (75.8/24.2 v/v) with 10 phr PET-co-5SIPA as compatibilizer (screw speed: 100 rpm, throughput: 4.5 kg/h), (c). PET/MXD6 (84.5/15.5 v/v) (screw speed: 200 rpm, throughput: 9 kg/h), (d). PET/MXD6 (84.5/15.5 v/v) with 10 phr PET-co-5SIPA as compatibilizer (screw speed: 200 rpm, throughput: 9 kg/h). The volume fractions of PET and MXD6 were calculated according to the shear viscosity values of the materials after extrusion (magnification x10000).

## DISCUSSION

Having a quasi co-continuous morphology in PET/MXD6 (75.8/24.2 v/v) blend without containing the compatibilizer and having a conventional droplet/matrix phase structure in PET/MXD6 (92.35/7.65 v/v) and 84.5/14.5 (v/v) blends clearly indicate the importance of material characteristics, processing conditions, additives, and moieties

of the blend components used for establishing the co-continuity. Even studies related to co-continuous morphology by using data obtained with rotational rheometer show the lack of Jordhamo equation since it only contains shear viscosity of the blend components. Nonetheless, the interfacial tension of the blend components, melt processing conditions, and viscoelastic nature of the phases are also of great importance for polymer blends and they all have to be involved when making calculations for determining the co-continuity point [6,19-21]. It should also be noted that using the viscosity data of the extruded neat blend components, i.e. PET and MXD6 for the calculation of the co-continuity point for a screw speed of 100 rpm has been shown to approach to this concept.

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