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Controlling the continuity and surface migration of conductive poly(ether-*block*-amide) in melt processed cast-film blends

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ABSTRACT

Polymer migration to the film surface during the melt processing of polymer blends is an important phenomenon, but has been limited in study. In this work, melt extruded cast films of conductive poly(ether-*block*-amide) (PEBA) with low-density polyethylene (LDPE) and polystyrene (PS) are prepared and the critical roles of phase continuity, interfacial tension and viscosity on PEBA surface migration are studied. When blended with high viscosity LDPEs, PEBA tends to migrate to the film surface, but significant surface enrichment only occurs at high PEBA continuities (typically > 50%). A possible surface migration mechanism based on the draining of PEBA through the connected networks is proposed and the migration process is facilitated by high interfacial tension. In compatibilized LDPE/PEBA and in PS/PEBA, the surface migration of PEBA is fully suppressed even at high continuity levels due to the low interfacial tension between the components. The surface resistivities of the binary blends are critically determined by the continuity of PEBA with a limited influence from surface enrichment. It appears that the continuity threshold to influence surface resistivity is lower than that for surface migration. A ternary LDPE/PS/PEBA blend with double percolation can simultaneously reduce the film surface resistivity and control PEBA surface migration by confining PEBA within a continuous low interfacial tension PS phase.

1. Introduction

The melt blending of polymers has been an effective approach to develop new materials in the past decades through combining favorable functionalities of the different components. Controlling the morphology and interfacial properties in polymer blends is crucial to tailor the performances of the final polymer blend product. However, polymer blending can also result in morphological variations between the surface [1–3] and the bulk [4,5].

Surface migration or surface enrichment of small molecule additives (such as plasticizers, processing aids, antistatic agents, etc.) in a polymer matrix has been long recognized (known as "blooming") [6–8]. A similar phenomenon can also occur in polymer/polymer mixers where one polymer tends to migrate to the surface/interface and segregate from the other one. Two main arguments have been proposed to explain the migration process in polymer systems. In the first case, it is believed that the polymer with a lower surface energy will migrate to the polymer/air interface in order to minimize the total free energy of system [1,9,10]. The second argument regarding the surface migration phenomenon involves configurational entropy. Large molecules are expected to suffer more of an entropic penalty at a rigid surface, and thus without significant enthalpic driving forces the low molecular component tends to partition at the surface [11,12].

Most of the previous work examines surface migration/enrichment in polymer blends prepared by solvent casting or spin coating after solution mixing and annealing is generally applied to highlight the thermodynamic influence [10–15]. Only a few studies have been carried out to examine the phase migration of polymer blends in melt processing where a flow field is present [3,16,17]. Lee and Archer studied the shear-induced migration in a polyethylene/polyethylene-*co*-methacrylic acid (PE/PE-co-MA) blend, and with a sufficiently long residence time they found that a significant surface enrichment of the low viscous PE-co-MA was obtained despite the very similar surface tension for the polymer pair [16]. Kolahchi et al. blended polyethylene glycols (PEGs) with a polyethylene terephthalate (PET) matrix to improve the hydrophilicity of the PET films [3]. Addition of a lower molecular weight PEG to PET results in a lower water contact angle which was attributed to the facile

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surface migration of smaller PEG molecules in the PET matrix. Furthermore, when a third immiscible component PS was added to the PEG/PET system, the migration of PEG to the film surface was enhanced. Fellahi et al. reported that, in a PE/PA (25/75 vol%) blend after injection molding, the component composition in the skin was found to be similar to that in the bulk independent of compatibilization [18]. In another study, Bhatia et al. examined surface composition of injection-molded poly (phenylene ether)/polyamide (PPE/PA) and PPE/high impact polystyrene (HIPS) blends using X-ray photoelectron spectroscopy (XPS) [19]. PPE and HIPS are miscible with similar surface tensions, and the composition on the surface was found to be identical to the bulk formulation of the blend. In the immiscible PPE/PA system, although no difference in surface and bulk composition was detected when the concentration of PA is ≤ 25 wt%, a significant surface enrichment for PA abruptly occurred at higher PA concentrations (≥30%). Based on the results, the authors proposed that in the immiscible blend the surface tends to be dominated by the continuous phase. However, it is not clear why nearly identical surface and bulk compositions were observed in the study when PPE is the continuous phase (PA wt% ≤ 25) (which should dominate the surface properties accordingly). As mentioned above, uniform surface and bulk composition was also reported by Fellahi and co-workers in the PE/PA system [18]. Thus, there is a clear need for a further understanding of the parameters controlling surface migration in the melt processing of polymer blends.

PEBA is an ionically conductive polymer (also known as inherently dissipative polymers) widely used in industry for charge dissipation applications [8,20,21]. After blending with conventional polymers, PEBA can form three-dimensional (3D) percolation structures at certain concentrations throughout the blend to dissipate static electricity.

In this work, we systematically study the influence of matrix viscosity, continuity and interfacial tension on the surface migration of PEBA in extrusion processing. Cast films of LDPE/PEBA (high interfacial tension system) and PS/PEBA (low interfacial tension system) are prepared by using a twin-screw extruder. The effect of continuity/morphology and surface migration of PEBA on the surface resistivity of the blends will be examined. An approach to control the surface migration of PEBA by confining PEBA within the low interfacial tension PS phase in a ternary blend of LDPE/PS/PEBA system will also be studied.

2. Materials and experimental

2.1. Materials

The general characteristics of the polymers used in this study are presented in Table 1. The PEBA is a segmented block copolymer of polyamide 12 (PA12) and polyethylene oxide (PEO). The copolymer is composed of 45% PA12 and 55 wt% PEO and contains 10–20 blocks of each component [22]. The conductivity in the copolymer originates from the water molecules absorbed in the PEO domains [23,24]. EAM is a random terpolymer of ethylene, butyl acrylate (6%) and maleic anhydride (3%). PEBA and EAM were dried in a vacuum oven at 60 °C for 48 h before processing and the other materials were used as received.

2.2. Rheology

The polymers were made into disk-shape samples through compression molding. The rheological properties were examined on a MCR 301 rheometer (Anton Paar, Austria) using a parallel-plate configuration with a gap of 1 mm. Small amplitude oscillatory shear (SAOS) tests for all the polymers were performed with a strain of 5–10% which is within the linear viscoelastic region as confirmed in a previous strain sweep test.

2.3. Melt blending

The blends were dry-mixed and then melt-processed on a co-rotating twin-screw extruder (TSE) (Leistritz ZSE 18HP) with a screw L/D ratio of 40. A temperature setting of 180/200/210/220/220/220/220/220/220 (die)°C and a screw speed of 100 rpm were applied. A slit die with a width of 25 cm and a gap of 300 μm was attached at the end of the extruder to prepare cast films. With a draw ratio of ~3, the thickness of the produced films is within 100 ± 10 μm. The cast roll was operated at room temperature and an air knife was placed right after the die to cool down the film.

2.4. Selective extraction and continuity

Film samples of about 100 mg were immersed in 20 mL hot formic acid solutions (50 °C) to selectively extract the PEBA phase. The extraction process was performed for 3 days and the solvent was refreshed 3 times. The resulting samples were then washed by methanol and dried at 80 °C under vacuum until a constant weight was reached. The weight of the samples was measured before and after extraction to calculate the continuity of the PEBA phase according to the following formula:

$$\text{Continuity (\%)} = \frac{w_1 - w_2}{w_0} \times 100\% \tag{1}$$

where w_1 and w_2 are the sample weights before and after the extraction of PEBA, respectively. w_0 is the total PEBA weight in the sample as calculated from the formulation.

2.5. Morphology characterization and analysis

The surface and bulk (cross-section) morphology of the film sample was examined by a JEOL JSM 840 scanning electron

Table 1
Characteristics of the polymers.

Polymers	Manufacturer/ Grade	T_m[a]	Zero-shear viscosity (Pa·s) (220 °C)[b]	Complex viscosity at 300 s^{-1} (Pa s) (220 °C)[c]
PEBA	Arkema/Pebax MV 1072	158 °C	250	150
PS	Americas Styrenics/MC3650	99.0 °C (T_g)	1608	206
LDPE-H	Total/1008	116 °C	13553	286
LDPE-M	Total/1022	109 °C	4242	222
LDPE-L	Total/1200	106 °C	504	84
EAM	Arkema/Lotader 3210	107 °C	–	–

[a] Data from the Material Datasheets.
[b] Estimated by applying the Cross model.
[c] Obtained from the data in Fig. 1.