ABSTRACT

Resistance-to-flow Analysis in Low Density Polyethylene/Plasticized Starch Blends Containing Compatibilizers with Attractive and Repulsive Interactions

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Processing of polymer blends is mainly controlled by the behaviour of their components, interfacial area and strength. Therefore, many experimental and theoretical investigations have been devoted to elucidating their basic governing principles. Nonetheless, there are only limited data in the literature about the effect of compatibilizers on the rheological properties of blends. The resistance-to-flow of low density polyethylene/plasticized starch blend and their compatibilized versions with poly(ethylene-r-vinyl acetate), maleated poly(styrene-ethylene-butadiene-styrene) and maleated polyethylene was investigated with a capillary rheometer at different temperatures. Furthermore, the melt elasticity enhancement of the aforementioned alloys was compared with their non-compatibilized polyethylene/thermoplastic starch blend via rheomechanical spectroscopy at 190°C and 500 Hz as an index of their interfacial strength. The results showed that by lowering the temperature of the melt alloys, the compatibilizer was directed toward interfacial localization and led to concomitant elasticity enhancement in comparison with their virgin blends. In addition, the resistance-to-flow of the blend and their alloys through capillary rheometer were enhanced and distinctively differentiated. This was attributed to the blend positive $\chi$ parameter which pushes compatibilizers localization at the interface with different adsorption densities and conformational resistance against flow of the system. In other words, a quasi core/shell structure formation at the dispersed phase/matrix interface was proposed as the origin of resistive capillary flow, leading to a viscoelastic loss enhancement. In analogy with Gent-Schultz equation governing the joint adhesion energy of polymers, the energy loss during capillary flow of a multicomponent blend was correlated for the first time to their interfacial strength. Interestingly, the calculated energy loss for the investigated melt blend and its compatibilized alloys in capillary flow was proportional to the solid state deformation loss during peeling of a corresponding joint interfaces reported by our group.

INTRODUCTION

Polymer blending has expanded the accessible properties and applications of these materials to mankind in such a way that nowadays most commercial products are made of polymers and alloys [1]. On the other hand, rheology plays a key role in technological developments of polymer alloys due to its determinant effects on their processing and solid state mechanical properties [2-4]. Therefore, understanding this phenomenon specifically in a melt with sophisticated compo-
nents organization has attracted the attention of many research groups [3-5]. The basis of polymer melt flow is mainly thermally activated chain reptation inside its surrounding tube via its *gauch to trans* transition along the chain axis [6]. In polymer blends, however, melt flow depends not only on their components behaviour but also on their morphological aspects namely interfacial area and strength. The flow of one phase system, for example, is controlled by the minor component effects in either facilitating or imposing barrier against the motion of the major component. In other words, addition of a miscible plasticizer to a polymer facilitates its flow due to diluting the surrounding tube of each chain [7]. But, polymer blends are often specifically an organized two phase materials through added compatibilizers or coupling agents. Accordingly, the flow of the system depends mainly on either simultaneous loading of both components or the matrix deformation and its transfer through the interface to the dispersed phase [8-10].

Block and graft copolymers are often applied to polymer blends to enforce certain organizational and morphological stabilizations. Therefore, numerous fundamental studies are focused on the use of A-B diblock copolymers for organizing (or compatibilizing) mixtures of A and B homopolymers [8-12]. In this case, there is no affinity or attractive interactions between surfactant and the homopolymers; as the A and B blocks exhibit athermal interactions with A and B homopolymers, respectively [13].

Nonetheless, a symmetric A-B surface active agent application to organize some critically two phase polymer blends with weakly segregated structure has limited performance (and they are only effective for $\chi_{AB}^N$ region slightly greater than 2 ($\chi$ is the Flory-Huggins interaction parameter for chains A and B, and N is the repeating units number for homopolymer chain). There are large regions of parameter space where A-B copolymers are not effective surfactant. For example, addition of diblock A-B copolymers to blends with $\chi_{AB}^N$ much greater than 2 led to formation of third micelle phase instead of its localizing at the interface [14]. Accordingly, in designing polymeric surface active agents, there seems a great need to some new strategic proposals. For example, an application of block copolymers with adsorptive interaction with one or both immiscible homopolymers can be mentioned [15,16].

In this article, a random copolymer, a functionalized homopolymer and a functionalized triblock copolymer have been used to compatibilize immiscible blends of low density polyethylene and thermoplastic starch. Polar monomer in random copolymer and functional groups in homopolymer and triblock copolymer, C, were selected to form attractive interactions with different strengths with thermoplastic starch (A) and repulsive interactions with the low density polyethylene (B). This approach resembles surfactant applications to the water/oil interfaces in which hydrophilic and hydrophobic portions of the molecule form attractive and repulsive interactions with water and oil, respectively [17]. Therefore, the main parameter in organizing A/B/A-C blends is the behaviour of surfactant with both attractive and repulsive interactions in both immiscible homopolymers. On the other hand, the trial and error approach in designing A-B surfactant does not work in A/B/A-C systems because of broadness of the $\chi$ parameter space.

In this research work, resistance-to-flow and elasticity enhancement of a low density polyethylene (PE)/thermoplastic starch (TPS) blend due to their temperature reduction or compatibilization by EVA, maleated polyethylene (PE-g-MAH) and maleated poly(styrene-b-ethylene butadiene-b-styrene) (SEBS-g-MAH) were investigated by flow through a capillary rheometer and rheomechanical spectroscopy. In addition, the possibility of resistance-to-flow prediction of a blend based on its components interfacial strength and bulk loss function was evaluated.

### EXPERIMENTAL

#### Materials

Low density polyethylene (Poliran LF-0020) was received from Bandar Imam Petrochemical Company (Iran). Glycerol (G-101, Shiminab Co.) and deionized water (Kimidaroo Co.) were used as starch plasticizers. Poly(ethylene-r-vinyl acetate) containing 28 mol% vinyl acetate (EVA-910, Hyundai Seetec Co.), maleated polyethylene (Admer NF-528, Mitsue Co.) and maleated styrene-ethylene-butadiene-styrene triblock copolymer (Kraton 1901-X, Shell Co.) were
used as compatibilizers. Commercial wheat starch was purchased and used as received.

**Preparation of Thermoplastic Starch**

Wheat starch powder was swelled under 2 atmosphere of argon pressure at 120°C with half of its plasticizers (the TPS contains 50 wt% of plasticizers). Then, the rest of the plasticizers was added to the swelled starch powder and mixed under appropriate conditions [18]. The final composition of the thermoplastic starch was characterized by thermogravimetrical analysis with TGA (DuPont 983) via heating the sample from 0-600°C with a rate of 10°C/min.

**Blend Preparation**

To locate the compatibilizers at the LDPE/TPS interface, 3.3 or 5.75 wt% of each were melt blended in a 60 mL internal mixer (Brabender, PL 2100, Germany) with a filling factor of 0.75 at 210°C and 60 rpm for 6 min. Then, 35 wt% of the TPS/compatibilizer blend was mixed for 6 min at 60 rpm and 190°C in the aforementioned mixer with PE.

**Resistance-to-flow Measurement**

The resistance-to-flow of PE/TPS and its compatibilized versions were measured with a capillary rheometer (Utility Model, Daven Test Ltd., UK). The experiments were run under 2.16 kg of weight at 140, 165 and 190°C and the melt flow analysis was performed gravimetrically with 0.001 g of precision. For each sample, five replicas were used and the average values with standard deviations of 15% were reported in Table 1.

**Rheo-mechanical Spectroscopy**

Rheo-mechanical spectroscopy of the blend and its alloys were performed by RMS-900 (Paar Physica Co., Germany) in a parallel plate geometry with 25 mm in diameter and a gap of 1 mm, and the corresponding data presented in Table 1.

**RESULTS AND DISCUSSION**

Figure 1 shows resistance-to-flow ($R_f$) or reciprocal of melt flow index (MFI$^{-1}$) of PE containing 35 wt% of TPS and its compatibilized versions with 3.3 wt% of EVA, SEBS-g-MAH and PE-g-MAH versus measurement temperatures. As one can observe, two parameters of the used compatibilizers and measurement temperatures affected the resistance-to-flow of PE/TPS blend. By adding EVA as compatibilizer, the resistance-to-flow at 190°C decreased while application of SEBS-g-MAH or PE-g-MAH increased $R_f$. In addition, the resistance-to-flow enhancement was higher for PE-g-MAH compatibilized blend compared to SEBS-g-MAH blend. While, the EVA had a very high MFI (360 g/min at 190°C and 2.16 kg

| Table 1. Rheomechanical data analysis of PE, TPS, PE/TPS blend and their compatibilized versions. |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|
| PE | TPS | PE/TPS | PE/TPS/EVA | PE/TPS/SEBS-g-MAH | PE/TPS/PE-g-MAH |
| G’ (10^4 Pa) at 500 s⁻¹ | 10.3 | 18.8 | 9.23 | 8.20 | 11.65 | 9.76 |
| G’ (10^5 Pa) at 0.1 s⁻¹ | 2.18 | 567 | 7.71 | 5.94 | 4.10 | 3.35 |
| η’ (10^4 Pa·s) at 0.1 s⁻¹ | 11.1 | 347.0 | 30.30 | 24.1 | 24.3 | 23.1 |
| MFI (g/10min) at 190°C | 2 | 11 | 4.10 | 4.31 | 2.59 | 3.35 |
| MFI (g/10min) at 165°C | - | - | 1.55 | 1.6 | 0.995 | 1.26 |
| MFI (g/10min) at 140°C | - | - | 0.69 | 0.62 | 0.412 | 0.49 |
Figure 1. Resistance-to-flow ($R_f$) of PE/TPS blend (×) and its compatibilized versions with 3.3 wt% of EVA (+), SEBS-g-MAH (♦), and PE-g-MAH (■) versus measurement temperatures.

Weight), PE-g-MAH and SEBS-g-MAH had much lower MFI of 2.2 and 0.45, respectively. It is noteworthy that similar to surfactants, each compatibilizer dissolves molecularly in the matrix up to a threshold concentration namely critical micelle concentration (CMC). Accordingly, dissolvable low molecular weight compatibilizers facilitate blend flow behaviour. But, raising the compatibilizer concentration above its CMC leads to its localization at the bi-phasic interfaces. The main driving force for compatibilizer localization at the blend interface is energy minimization of the system. In other words, blend temperature reduction increases its free energy where it can be compensated by increasing the compatibilizer loading leading to its interfacial localization [13,14]. Therefore, it seems that addition of 3.3 wt% of EVA to the PE/TPS blend at 190°C was below its CMC while the same amount of other two compatibilizers stayed above their CMC.

Consequently, EVA was dissolved in the melt blend at this concentration while PE-g-MAH and SEBS-g-MAH were localized at the interface of the blend components. In addition, PE-g-MAH is the most efficient compatibilizer among three in rising alloys resistance-to-flow. In other words, compatibilizer localization at the interface led to interfacial area increment and raised the resistance-to-flow. Here, the polar part of each compatibilizer molecule forms attractive interactions with the dispersed phase particles and simultaneously leaves their hydrocarbon part to diffuse into the PE matrix. This leads to the formation of a quasi core-shell structure from the dispersed phase and the attached compatibilizers where it diminishes the direct interaction between the matrix.

Figure 2. Schematic representations of dispersed TPS particles in the PE matrix (a), and localization of various compatibilizers: (b) EVA, (c) SEBS-g-MAH, and (d) PE-g-MAH.
and dispersed phase. Therefore, the contribution of the localized compatibilizer on the system flow depends on interfacial morphology and specifically on its structure. A schematic representation of the TPS dispersed particles in the PE matrix at 190°C was illustrated in Figure 2a. Addition of the required amount of compatibilizers to pass their CMC from EVA, SEBS-g-MAH and PE-g-MAH changed the dispersed phase morphology as depicted in Figures 2b, c and d, respectively. The peculiar form of the EVA localization at the interface, zigzag layering, is the direct result of random distribution of polar and non-polar monomers along the copolymer chain [19]. On the other hand, high molecular weight SEBS-g-MAH (with low MFI) led to its reactive interactions through maleated ethylene-butylene blocks to the TPS and left its styrenic blocks to interact with the matrix chains. At last, a maleated high molecular weight PE was tethered to the dispersed phase particles via its polar group attractive interactions while its long hydrocarbon moiety diffused and formed entanglements with the PE matrix chains. Accordingly, addition of enough EVA, SEBS-g-MAH and PE-g-MAH to the PE/TPS blend enhances its resistance-to-flow due to interfacial strengthening via shell/matrix interactions. It deserves re-emphasizing that shell/ matrix interactions are formed through threading of EB block in SEBS-g-MAH and entanglement of hydrocarbon moiety of PE-g-MAH with the matrix chains.

Figure 3 presents the resistance-to-flow of PE/TPS blend and its compatibilized versions with 5.75 wt% of EVA, SEBS-g-MAH and PE-g-MAH at three different temperatures. Even though some similarities with the results of Figure 1 can be observed, some interesting differences are noticed too. First of all, by increasing the concentration of EVA to 5.75 wt% of the TPS the behaviour of melt blend at 190°C changed from resistance-to-flow decrement of Figure 1 to a slight increment. This was attributed to the EVA critical micelle concentration crossing, its adsorption to the interface and contribution in resistance-to-flow increment. Second, a close look at resistance-to-flow of compatibilized samples containing different amounts of polymer surfactants via re-plotting their data points in a combined way illustrates their efficacy differences (Figure 4). In other words, by raising the amount of SEBS-g-MAH and PE-g-MAH, the system resistance-to-flow increases due to dispersed phase size decrement and its resultant interfacial effects magnification. This structural evolution is stronger in PE-g-MAH in comparison to SEBS-g-MAH because the former is more efficient in interfacial coverage and resistance to flow enhancement. In

Figure 3. Resistance-to-flow (Rf) of PE/TPS blend (×) and its compatibilized versions with 5.75 wt% of EVA (+), SEBS-g-MAH (▲), and PE-g-MAH (■) versus measurement temperatures.
other words, by adding 3.3 wt% of PE-g-MAH and then raising its amount to 5.75 wt% the slope of resistance-to-flow increment decreases while it still increases in SEBS-g-MAH compatibilized blend. On the other hand, 3.3 wt% of EVA was insufficient to cross its CMC but its increment to 5.75 wt% changed its behaviour from a flow facilitator to a retarder.

In addition, a temperature decrement caused $\chi N$ enhancement where the compatibilizer localization is directed at the interface, which result in another resistance-to-flow increment mechanism (Figure 3). In other words, a quasi core-shell structure is formed from the dispersed phase and tethered compatibilizers inside the matrix where there is a resistance against flow.

To reach a better understanding of the role of compatibilizer in organizing various phases and specifically its interfacial effects on system resistance-to-flow, a rheomechanical spectroscopy was also employed at 190°C as a function of the frequency (Figure 5). By increasing the applied load frequency, the PE/TPS melt blend changed toward a rubbery behaviour via an increment in its components elasticity and structural stability. The rheo-mechanical data analysis of PE and TPS melt blend and their compatibilized versions are presented in Table 1. To characterize the role of melt structure, specifically its interface on non-linear viscoelastic deformation, the correlation of resistance-to-flow versus melt dynamic elasticity, $G'$, at 500 Hz and 190°C was considered (Figure 6). As one can observe, the addition of 3.3 wt% of PE-g-MAH or SEBS-g-MAH to the melt blend of PE and TPS enhances melt elasticity and its resistance-to-flow at various temperatures. This was attributed to the formation of a biphasic structure and localization of the compatibilizer at the interface rising melt elasticity and resistance-to-flow. Addition of EVA, however, at least at 190°C and 165°C led to elasticity decrement and negligible resistance-to-flow increment due to its dissolution in the components instead of localization on their interface. It is clear that the flow fields in rheomechanical analysis and capillary rheometry are very different.

Figure 4. Resistance-to-flow ($R_f$) of compatibilized blends with different amounts of compatibilizers; EVA ($+$), SEBS-g-MAH ($\triangleright$), and PE-g-MAH (■).

Figure 5. Rheomechanical spectroscopy of PE/TPS blend at 190°C as a function of the frequency.

Figure 6. The resistance-to-flow ($R_f$) of PE/TPS blend ($\times$) and its compatibilized versions; EVA ($+$), SEBS-g-MAH ($\triangleright$), and PE-g-MAH (■) versus melt dynamic elasticity, $G'$ at 500 Hz, and at three temperatures from bottom to top 190, 165, and 140°C, respectively.
In other words, motion of a bi-phasic system in linear viscoelastic region is limited to molecular scales. While, non-linear viscoelastic deformation in capillary flow causes tumbling of the quasi core/shell structure of the dispersed phase with their attached compatibilizers leading to higher required stress. Therefore, a blend with enough compatibilizer in a linear viscoelastic and capillary flow fields generate higher elasticity and resistance-to-flow due to their interfacial structuring, respectively.

It should be emphasized that the role of compatibilizer in energy dissipation during deformation of a multicomponent system is magnified via temperature decrement towards its solid state. In other words, by reinforcing the interface of two phases in the melt state the required energy for its processing decreased to a minimum, while temperature decrement toward solid state increased it to a maximum. Temperature decrement derives the compatibilizer to the interface due to $\chi_N$ increment where the stress is transferred to the matrix and magnifies the barrier against motion of the dispersed phase leading to a large amount of energy dissipation. In other words, resistance-to-flow of systems compatibilized with PE-g-MAH and SEBS-g-MAH increased mainly through energy dissipation by temperature decrement. Polymer joint deformation energy in solid state was also studied and correlated to its interfacial thermodynamic energy by pioneering work of Gent and Schults [22] and quantified as follows:

$$G = W_0 (1 + \varphi) \quad \text{(1)}$$

where $G$, $W_0$ and $\varphi$ are practical work of adhesion, thermodynamic work of adhesion and joint viscoelastic loss function, respectively [23]. Therefore, defining a similar correlation between the interfacial strength of melt phases and its resistance-to-flow, in analogy, can be fruitful. Consequently, the melt loss function of the samples was inferred, analyzed and compared with their solid state deformations loss function. Multi-phase material melt elasticity involves with its components and interfacial elasticity originating from bulk and interfacial molecular interactions, respectively. Therefore, the interfacial elasticity can be estimated through subtracting the blend elasticity from its corresponding alloys, $\Delta G\prime = G\prime_A - G\prime_B$.

Accordingly, resistance-to-flow can be correlated with interfacial elasticity, analogous to the thermodynamic work of adhesion, as follows:

$$R_f = \text{MFI}^{-1} = \Delta G\prime (1 + \varphi\prime) \quad \text{(2)}$$

According to the EVA localization at the interface as two other compatibilizers at 140°C the $R_f$ data at this temperature, and $G\prime$ of PE/TPS and their compatibilized versions were used to calculate the melt loss function (eqn 2). Then, the joint loss function for PE/TPS and their compatibilized versions in peel experiment [24] were plotted versus the melt viscoelastic loss function of corresponding alloys (Figure 7). To consider the role of glycerine in compatibilization of PE and starch [25] a reference value was assigned to their interfacial elasticity and used in place of the PE/TPS elasticity. As one can observe, the loss function during peeling experiment in solid state is proportional to flow dissipation in melt state with corresponding alloys. However, in case of EVA compatibilized blend the melt state loss function is much higher than what was expected, based on corresponding solid sample. This was attributed to $G\prime$ determination at 190°C where would be much higher at lower temperatures leading to $\Delta G\prime$ enhancement and $(1+\varphi\prime)$ decrement. In addition, low molecular weight of the used EVA even at the interface may facilitate flow instead of retarding it and raising the energy dissipation.
CONCLUSION

Resistance-to-flow measurements in PE/TPS melt blend and its compatibilized versions with EVA, SEBS-g-MAH and PE-g-MAH at various temperatures and their comparisons with rheomechanical spectroscopy data of corresponding samples at 500 Hz and 190°C resulted in following achievements. First, melt temperature decrement magnifies the role of components organization due to addition of compatibilizers in resistance-to-flow and melt elasticity decrement. Second, the energy loss in melt under high shear of capillary flow showed a meaningful dependence on their structural stability defined by their rheomechanical $\Delta G'$ at highest frequency. Third, the extrapolation of the melt energy loss toward its solid state through temperature was proportional with the peel loss energy measured at its solid state. Finally, an equation similar to the Gent-Schultz in polymer adhesion was proposed among the resistance-to-flow, interfacial melt elasticity and melt energy loss function.

REFERENCES


