

Full Length Research Paper

A complete elimination of discontinuity in the flow curve of the thermoplastic vulcanized (PE/PB) by maleated polyethylene

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Thermoplastic vulcanized polybutadiene/high density polyethylene (TPV) (70/30) was prepared using organic peroxide (3%) as vulcanizing agent. A maleated polyethylene (MAPE) was prepared by melt mixing. The percent of maleation found was (1.78%). The percent of maleated polyethylene added to the (TPV) was (0, 2, 4, 6, 8 and 10). The rheological properties were measured at temperature of 140°C. Discontinuity of the shear stress vs. shear rate curve appeared for 0, 2, 4 and 6% of the MAPE. While for 8% of the MAPE, the curve was continuous with concavity at the second critical shear stress (τ_2) and a complete elimination of curve discontinuity was reached when using 10% MAPE.

Key words: Polymer melt instabilities, thermoplastic vulcanized, polymer rheology.

INTRODUCTION

Melt flow instabilities, loosely referred to as "melt fracture," are phenomena limiting polymer extrusion. The general trend in the development of flow instabilities during extrusion of polymer melts involves the absence of extrudate surface distortions at relatively low shear rate/stress values (at which presumably the wall slip velocity is negligible) on one hand and at relatively very high shear rate/stress values at which correspondingly high (and presumably stable) wall slip velocities exist. This suggests that extrudate distortions are less likely to occur under conditions in which a stable flow boundary condition exists at the wall; whether it is either a stable wall stick or stable wall slip condition. The occurrence of these instabilities for plastics is known at least since 1945 (Rudolf and Molenaar, 1998). The "sharkskin effect" in polymer extrusion was the first instability to occur and thus it is the first problem that must be solved, before one needs to worry about the other instabilities. The manufacturing of plastics is one of the most important industrial manufacturing processes, and is used to create a huge variety of objects (rods, wire, sheet, fiber and

others). The most common process is extrusion, in which polymer fibers or sheets are produced by forcing the polymer melt or solution through a cylindrical hole or slit (a "die") (Denn, 2001). Flow instabilities that occur in melt processing arise from a combination of polymer viscoelasticity and the large stresses that occur and cause large, rapid deformations. This is in contrast to flows of Newtonian fluids, where inertia and surface tension is usually the driving forces for flow instabilities. Both the elasticity and the high stresses that occur in the flow of molten polymers arise from their high molecular weight (that is, from the enormous length of their molecules). The high stresses are associated with the high viscosity of molten commercial thermoplastics and elastomers. Typical values range from 10^3 to 10^6 Pa s, whereas the viscosity of water is about 10^{-3} Pa s.

An easily observed manifestation of melt elasticity is the large swell in cross section that occurs when a melt exits a die. There are several common themes that emerge in the various extrusion instabilities and consequent techniques for their elimination. For example, wall slip plays a prominent role in sharkskin, stick-slip, and in the use of additives to provide stable flow. Processing aids (PAs) are frequently used. The PAs eliminate flow instabilities or postpone them to higher flow

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rates. The end result is an increase of the productivity as well as an energy cost reduction while, high product quality is maintain edge (Evdokia et al., 2002). The melt fracture of LLDPE was studied by (Denn, 1990; 2001) and found that the surface of the extrudate becomes visibly rough at a wall shear stress level that is typically of the order of 0.1 MPa, with apparent periodicity in the small-amplitude distortion; this phenomenon is commonly called sharkskin. At a higher level of stress, typically of the order of 0.3 MPa, the flow becomes unsteady and the extrudate alternates between sharkskinned and smooth segments; this is commonly called stick-slip or spurt flow. At still higher stress levels, sometimes after a second region of spurt flow, the flow becomes steady. The extrudate surface is relatively smooth during the early part of this steady regime, with a long-wavelength distortion, but gross distortions occur at higher stresses; this regime is commonly called wavy or gross melt fracture.

EXPERIMENTAL

Materials

High density polyethylene (HDPE) SCPILEX 5502 and low density

High density polyethylene (HDPE) SCPILEX 5502 and Low Density Polyethylene (LDPE) SCPILEX 464 were supplied by state company for petrochemical industry (SCPI) in Basra (MFI=0.46 gm/10min, density=0.953 gm/cm³ and MFI=4.0 gm/10min, density=0.9220 gm/cm³ respectively). Polybutadiene was obtained from Malaysian company with (Mooney viscosity ML (1 + 4) at 100°C 45 ± 5). Maleic anhydride (MA) industrial grade was supplied by Adrash Chemicals and Fertilizers Ltd., Udhna Gujorat-India. Maleic anhydride was used without purification. 2- ethyl terbutyl-hexanoate peroxide (C67), peroxide content 98% was supplied by Pergon G.m.b.h Company.

Instrument

Rheological measurements

Rheological properties were carried out by using a capillary rheometer device (Instron model 3211), ASTM D-3835. The diameter of the capillary is 0.76 mm, the length to diameter (L/D) ratio of 80.9, with an angle of entry of 90°. Load weighing which dropped on the polymer melts by plunger transverse from the top to the bottom of the barrel was constant (2000 kg). The constant plunger speeds ranged from 0.06 to 20.0 cm.min⁻¹ and the extrusion temperature was 140°C.

Mixer instrument

Mixer-600 attached to Haake Rhechard Torque Rheometer supplied by Haake Company. The RPM of the Mixer can be controlled depending on the shear rate.

FTIR-measurements

Fourier transforms infrared spectrophotometer Shimadzu FTIR-

84005 was used for measuring the IR-spectra for the samples.

Polyethylene (PE)-maleic anhydride grafting

Low Density Polyethylene (LDPE) Grade 464 was fed to a Mixer-600 attached to Haake Record meter at temperature = 150°C and RPM = 64. After 5 min, maleic anhydride was fed portion wise and the peroxide was added drop wise. The modified polyethylene was characterized by FTIR and evaluated via the degree of maleation (%) according to (Ghaemy and Roohina, 2003; Moayad et al., 2008).

$$\text{Acid Number (mg KOH / g polymer)} = \frac{\text{ml KOH} \times \text{N KOH} \times 56.1}{\text{Polymer (g)}}$$

Therefore,

$$\% \text{MAH} = \frac{\text{Acid no.} \times 98}{2 \times 56.1}$$

$$\text{MAH} = 1.78\%$$

Preparation of the thermoplastic vulcanized (PE/PB)

Polybutadiene was feed to Mixer-600 at temperature =140°C and RPM = 32. The high density polyethylene and the maleated polyethylene mixed together before added to the Mixer-600, after two minute the peroxide was added. Then, the velocity of mixing was changed to RPM = 64 and the mixing time continue for 10 min.

RESULTS AND DISCUSSION

The comparison of the infra-red spectra of the pure polyethylene and the maleated polyethylene sheet, Figure (1a and b) has confirmed the presence of maleic anhydride units on polyethylene backbones. In comparison with the infra-red spectrum of pure polyethylene, the grafted polyethylene showed very strong bonds at 1779 and 1859 cm⁻¹, which are characteristics of cyclic anhydride. The band at 1221cm⁻¹ corresponds to C-O stretching vibrations in the cyclic anhydride (Ghaemy and Roohina, 2003; Moayad et al., 2008). The Flow curve instability phenomena for the TPV without compatibilizer agent (MAPE) were shown in Figure 2. From Figure 2, the flow curve was divided into four regions, the first region started at shear stress (168 - 179) KPa and shear rate (5.4 - 18 S⁻¹) the curve was smooth, the second region started at stress (229.4 - 319.2) KPa which was the first critical shear stress (τ_1) and shear rate (54 - 180 S⁻¹), there was fluctuation in the curve and sharkskin phenomena was observed (Moayad et al., 2008; Humberto et al., 2009; Humberto et al., 2010). The third region started at shear stress (364 - 403.2) KPa the second critical shear stress (τ_2) and shear rate (540 S⁻¹) there was pressure oscillation and stick-slip phenomena was observed (Denn, 2001), while the fourth region started at shear stress (476) KPa and shear rate (1800 S⁻¹) and melt fracture phenomena was observed.

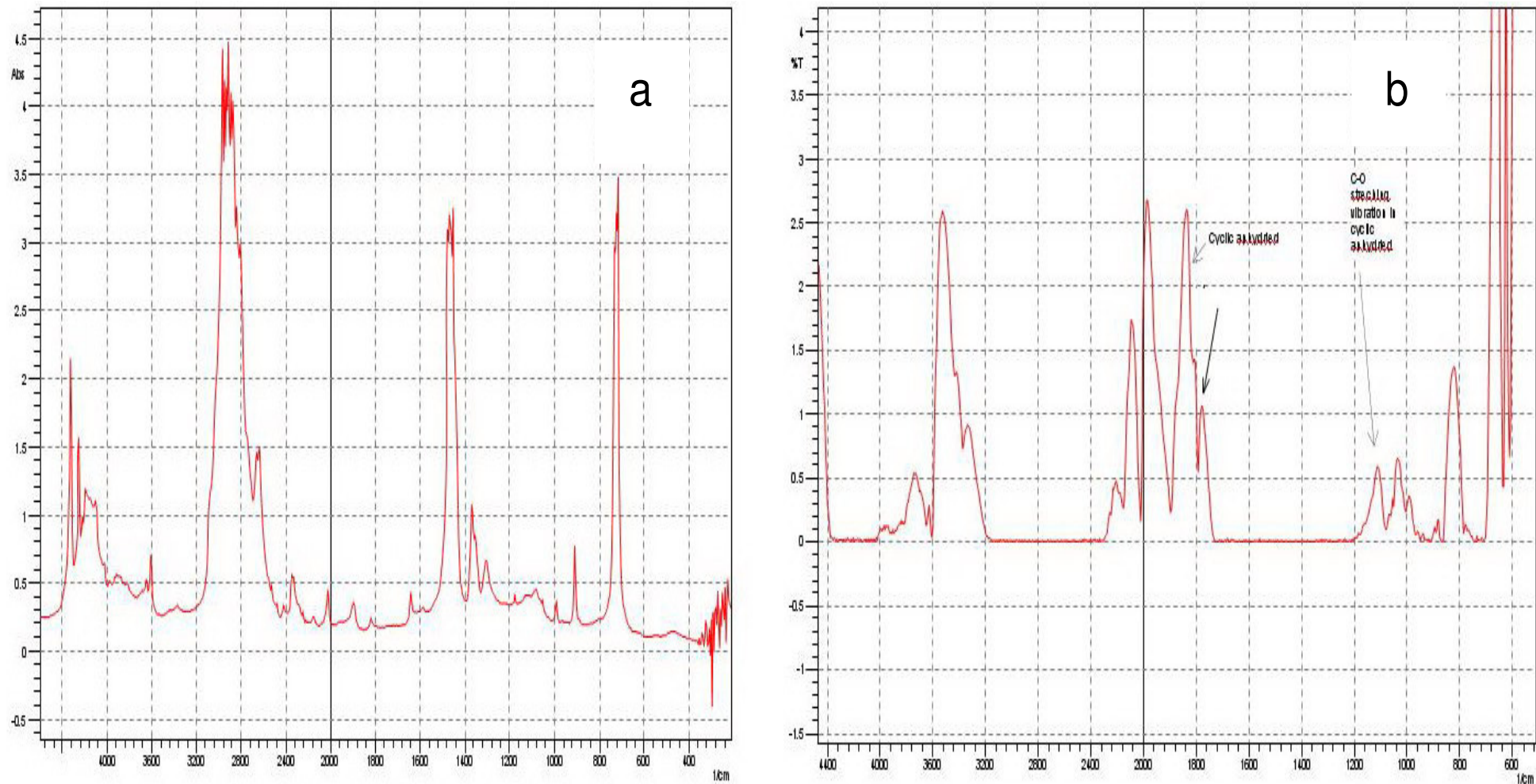


Figure 1. FT-IR spectra of A- polyethylene and B- Maleated polyethylene.

The fluctuation in flow curve due to the uncompatibility between the polymer blend and adding 2% of the MAPE as compatibilizer, the curve was linear (Figure 2) and the value of the shear stress was reduce to (235.2 - 285.6) KPa,

this behavior was attributed to the increase of the chain interactions between the two polymers. While, the second critical shear stress (τ_2) at shear rate 540 S^{-1} the value was reduced to (274.4 - 296.8) KPa, but the rheological distortion still

appeared because it was based on a stick-slip mechanism. It is purported (Ramamurthy, 1986; Lau and Schowalter, 1986; Jaewhan et al., 2009) that, above a critical shear stress, the polymer experiences intermittent slipping due to a lack of

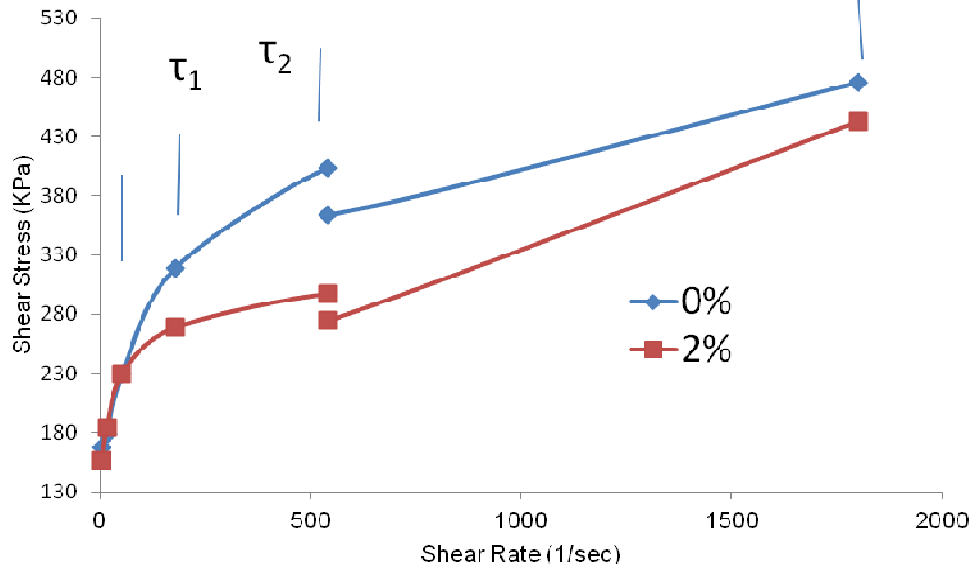


Figure 2. Flow curve of TPV at 140°C with: 0% (MAPE) and with 2% (MAPE).

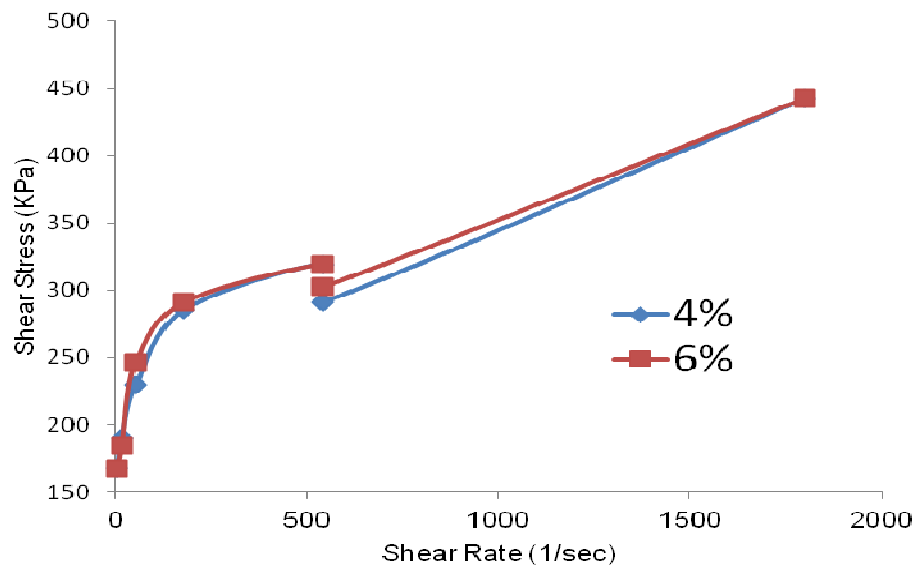


Figure 3. Flow curve of TPV at 140°C with: 4% (MAPE) and with 6% (MAPE).

adhesion between polymer and die wall, in order to relieve the excessive deformation energy adsorbed during the flow. There was pressure oscillation inside the capillary and discontinuity was appeared on the flow curve for the polymers blend with (4 and 6%) compatibilizer (MAPE) as shown in Figure 3.

While increasing the percent of the MAPE to 8% curve was linear and smooth as shown in Figure 4. The 8% was the sufficient quantity to provide the sufficient chains interaction between the two polymers blend but, not the sufficient adhesion force between the polymers

blend and die surface which causes appearance of concavity on the flow curve. While, the 10% compatibilizer (MAPE) was the sufficient quantity to achieve the chain interaction between the two polymer and the force adhesion between the polymers blend and the die surface. Result in the disappearance of flow instability curve of polymers blend. The increase in adhesion force is due to the presence of the carboxyl group and hydroxyl group of the maleic anhydride on the backbone of the polyethylene (PE), thus improved the adhesion property between the TPV and the die (Figure 5) (Moayad et al., 2008).

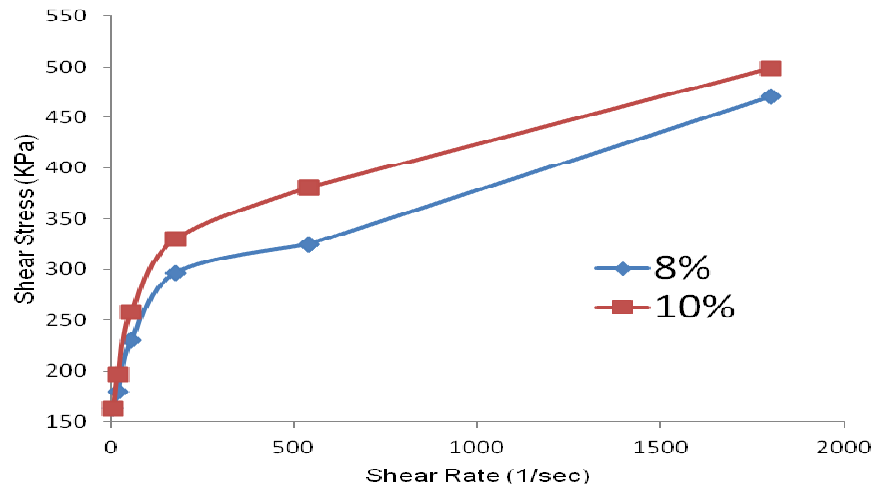


Figure 4. Flow curve of TPV at 140°C with: 8% (MAPE) and with 10% (MAPE).

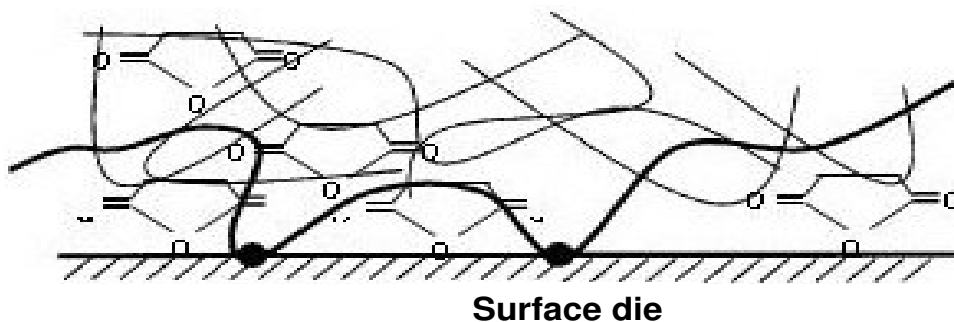


Figure 5. Schematic representation of maleic anhydride units on polyethylene backbones, which increases the adhesion force between the TPV blend and die surface.

Conclusion

The effect of compatibilizer (MAPE) to eliminate discontinuity in the flow curve of the thermoplastic vulcanized (PE/PB) was studied. Various concentration of the compatibilizer (0, 2, 4, 6, 8 and 10 wt/wt%) were tested. It was shown that the complete elimination of discontinuity which caused by the pressure oscillation inside the die during the polymer melt flow. The presence of the MAPE will act as compatibilizer between the two polymer chain and both the 8% and 10% can achieved the complete chain interaction and the blend will be completely miscible and act as one phase, while the 8% cannot offer the sufficient adhesion forces between the polymer and the die wall, for that there was concavity in the flow curve, which disappeared in the flow curve of TPV with 10% MAPE.

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