Novel Processing Aids for Extrusion of Polyethylene

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Commercially available thermoplastic elastomers (TPEs) based on block copolymers of diisocyanates and polyols (i.e., TPUEs) were used to delay sharkskin and stick-slip instabilities in the extrusion of linear low density polyethylene (LLDPE). When TPUE is added in a small mass fraction to LLDPE, it deposits at the die surface during extrusion and may postpone the onset of sharkskin instability to a 12–20 times higher rate of extrusion. Substantial delay of sharkskin was also achieved under conditions without slip of molten PE inside the die coated by TPUEs. Efficiency to delay the instabilities depends on elasticity of TPUE at processing temperature. The TPUEs could be a cost-effective substitution of fluorinated polymers such as processing aid, lubricant and release agent in the processing of polyethylene by extrusion, blow molding, and injection molding. J. VINYL ADDIT. TECHNOL., 11:127–131, 2005. © 2005 Society of Plastics Engineers

INTRODUCTION

Polyolefin resins are the world's fastest-growing family of polymers and there are good reasons for this: 1) cost/performance: modern polyolefins cost less to produce and process than any other plastics and materials they replace; and 2) they have an extremely low environmental impact.

A major part of polyolefin resins are polyethylene (PE) resins. The present revolution in plastics is the development of metallocene catalysts. Plastics made from metallocene catalysts are tougher, stronger, and cleaner than plastics made from conventional catalysts. The products manufactured with metallocene PE offer down-gauging opportunities to reduce costs and environmental pollution. Analysts forecast yearly production growth of more than 20% for metallocene-PE resins, reaching around 17 million tons in 2010, representing about one-fifth of all PE resins.

Metallocene-PE resins are particularly subject to various flow instabilities during processing by extrusion [1–5] and cannot be processed without the use of polymer processing aids (PPAs). The PPAs based on fluorinated polymers ("Viton," "Dynamar," and "Kynar") used to be the only option in the processing of PE resins. In spite of their inherently high cost, the fluorinated PPAs are used in the manufacture of blown films, cast films and sheets, blow-molded bottles and containers, extruded fibers, pipes, profiles, and cables because of the benefits from improved processability and quality of final products. The market for fluorinated PPAs is currently 100 MM Euro and the demand is growing quickly. In fact, the use of PPAs is limited only by the high cost of the fluorinated polymers.

The use of fluorinated polymers in the processing of polyethylene resins contradicts the generally lower environmental impact of metallocene-based plastics. Decomposition of the polymer blends containing fluorinated polymers results in the release of a hazardous gas. The gas, which contains fluorine, potentially induces cancer and contributes to the destruction of the ozone layer of our planet. We propose that instead of the fluorinated polymers some thermoplastic elastomers (TPUEs), based on block copolymers of diisocyanates, i.e., urethanes and polyols, be used as novel PPAs. TPUEs are already available at a price below 5 Euro per kilo, much lower than the price of fluorinated PPAs, and many of them are FDA compliant.

TPUEs are immiscible with PE resins and adhere well to metal oxides, glass, and ceramics. In processing of the blends based on PE resin with TPUE, the inclusions of TPUE come into contact with the metal parts and replace PE resin at the surface already in the mixing zone of an extruder. The additives accumulated at the wall slowly flow along the wall to the exit of the extrusion die so that the product surface is enriched by the additives. According to Zhou and Pozrikidis [6], the efficiency of separation of the TPUE inclusions will be higher if the TPUE is characterized by lower viscosity and the ratio of viscosities of the TPUE and of the matrix polymer exceeds 10. The presence of polar molecules at the product surface improves its printability, while TPUE molecules at the die surface change boundary conditions of the melt flow. The efficiency of TPUE as a processing aid is especially high if the die or the extrusion mold is made of glass, ceramics, or it has a coating enriched by oxides.

EXPERIMENTAL

Materials

The experiments were carried out using commercially available LLDPE "LL1201 XV" from ExxonMobil Chem-

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icals (Houston, TX). This material was selected for its clarity, its overall low level of additives, and the absence of PPA in its formulation. It is characterized by: density, 0.925 g/cm^3; melting point, 123°C; and melt index, 0.7. We used "Viton FreeFlow SC-PW" from DuPont (Rockville, MD) and "Dynamar-E-15653" from Dyneon (3M, St. Paul, MN) as "state of the art" fluorinated PPAs. These materials are referred to below as "Viton" and "D 15653." We used the following commercially available TPUEs: "E S50A," "E 685A," "E SP9269," which are TPUEs of a product family "Elastollane" from Elastogran; "TPSE 80," "TPSE 120," "TPSE 140," and "TPSE 160" of a product family "GENIOMER″ from Wacker Chemie (München, Germany); "Baymod-PU-A" from LanXess (Leverkusen, Germany); "P D15N70," "P D152 K," "P D162 K," "P D13 S," "P 45-50/25," "P D12C75," "P 45-50/22," "P 46-73/27," "P 46-73/32," and "P D12F75" are TPUEs of product families "Pearlthane," "Pearlstick," "Pearlcoat," and "Disperbond" from Merquinsa (Barcelona, Spain).

Instrumentation

"Rheotest RT-20" from Haake-Thermo was used to measure dynamic mechanical performance of the materials at 165°C. A ram extruder from Loomis with a barrel of 60 · 200 mm (diameter · length) and a hydraulically driven piston was used to extrude molten PE from a die. The piston velocity was controlled from a computer. Values of the pressure and of the piston position were digitized during extrusion and transmitted to the computer for recording. The die and the extrudate were illuminated by a stroboscope and were videorecorded by a camcorder at 25 frames/s. The stroboscope was synchronized with the camcorder and the videorecords were triggered simultaneously with the data records to get precise correspondence between them. Blow film from LLDPE was produced with a screw extruder "Polytest – 20T" from Schwabenthan-Maschinen equipped with a ring die 40 mm diameter and 0.5 mm gap width.

RESULTS AND DISCUSSION

The mechanical properties of TPUEs are characterized by a Young's Modulus $G = G1+iG2$, which is a complex value having elastic, G1, and viscous, G2, parts. We use the ratio G1/G2 as a criterion of elasticity. Molten PE is elastic at frequencies above 10 Hz, that is, $G1/G2 > 1$. For the processing of PE resins we classify TPUEs into two groups: "Lubricants" and "Adhesives." The reason for such classification will be clear from their behavior in blends with LLDPE. The "Lubricants" are elastic at processing temperatures and at frequencies of 10–25 Hz in comparison to molten PE. That is, their G1/G2 is larger than that of PE, while for the "Adhesives" the opposite is true. For illustration, the values of G1/G2 vs. frequency at a temperature of 165°C are presented in Fig. 1 for LLDPE "LL 1201 XV," for "Viton" and "D 15653," for TPUEs: "E 685A" and for "TPSE 160," which are "Lubricants"; and in Fig. 2 for LLDPE and for TPUEs: "P D15N70," "P D12F75," and "P D125K" which are "Adhesives."

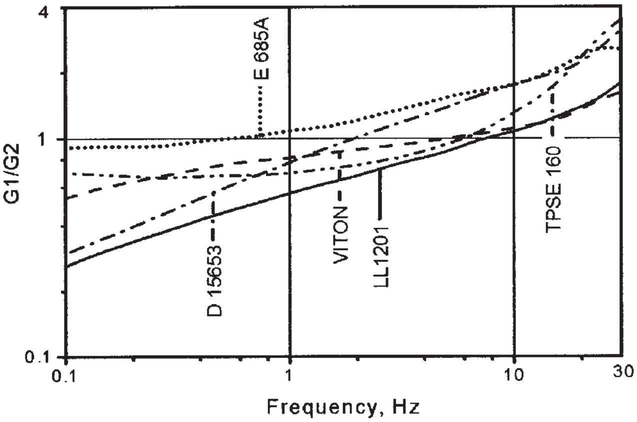

FIG. 1. Ratio of elastic to viscous modulus G1/G2 vs. frequency for "Lubricants."

Characteristic flow curves that are the curves of pressure at the die entrance vs. averaged (in the die cross-section) product velocity are shown in Figs. 3 and 4 for the tubular die 6 · 32 mm (diameter · length). For the use of "Lubricants" the die was precoated with a thin layer of "E S50A" (a dashed line in Fig. 3), "E 685A" (a dotted line), and "TPSE 160" (a dash-dotted line). For the use of "Adhesives" the die was precoated by "P D15N70" (a dashed line in Fig. 4), "D12C75" (a dotted line), and "P D12F75" (a dash-dotted line). In the technologically important range of extrusion from 2–100 mm/s the use of the "Lubricant" PPA shows lower pressure while the use of the "Adhesive" PPA makes very little difference in comparison with the uncoated die. Using either a "Lubricant" or an "Adhesive" may give at least a 10 times higher rate of extrusion in comparison with the use of the uncoated die. Product appearances are presented in Fig. 5 at sharkskin onset, in Fig. 6 at about 40 mm/s, and in Fig. 7 for blown film.

Our experimental results are summarized in Table 1. All data are normalized to those of virgin LLDPE. M = 5.4

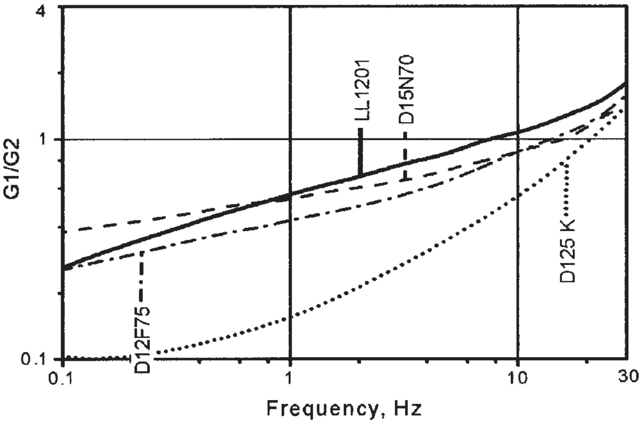

FIG. 2. Ratio of elastic to viscous modulus G1/G2 vs. frequency for "Adhesives."

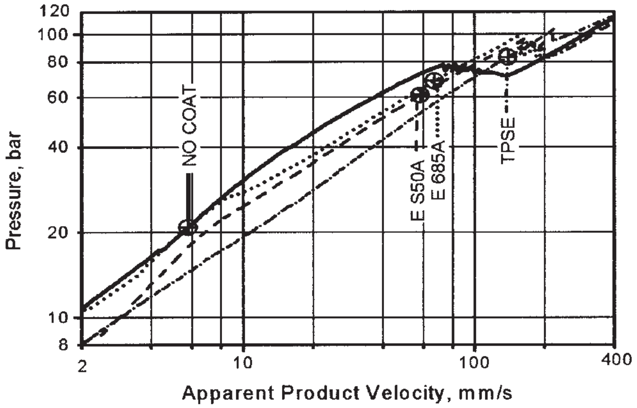

FIG. 3. Characteristic curves for extrusion with the steel die pre-coated by "Lubricants" (slip). Onsets of sharkskin are marked by crosses in circles. While these TPUEs are characterized by high surface energy in comparison to fluorinated PPAs the use of them results in slip and delay of sharkskin.

mm/s is the sharkskin onset in extrusion of virgin LLDPE with the use of an uncoated die, S = 90 mm/s is the velocity of stick-slip transition which corresponds to a step-like change in the characteristic flow curve, K = 1.4 is G1/G2, which is measured at 20 Hz for LLDPE, V = 16.8 is dynamic viscosity of LLDPE at 0.1 Hz in [kPa · s].

We prepared blends of "TPSE 140" and "TPSE 160," which are "Lubricants," as well as "P 46-75/32," "P D125K," and "P D12C75," which are "Adhesives" with LLDPE and extruded them to measure induction time and efficiency to inhibit sharkskin. The TPUEs were dissolved or swollen in organic solvents, distributed in a form of powder or droplets among granules of LLDPE, mixed and dried by a jet of compressed air, and molten in the barrel of an extruder. Experiments were carried out with the use of dies 3 · 24 mm made from quartz glass or stainless steel or brass coated by Pt. Induction time or a mass fraction of additives were about 5 times less in the case of the die made from glass in comparison with the use of the die from stainless steel having no oxide layer at the surface. With the use of low viscous "TPSE 160" and the die from glass 200 ppm of additives was enough to keep steady defect-free extrusion of "LL1201 XV." Induction time to inhibit sharkskin at product velocity 50 mm/s with 200 ppm of "TPSE 160" was less than 2 min. We did not suppress sharkskin with the use of a brass die with Pt coating even for a mass fraction of additives 2,000 ppm.

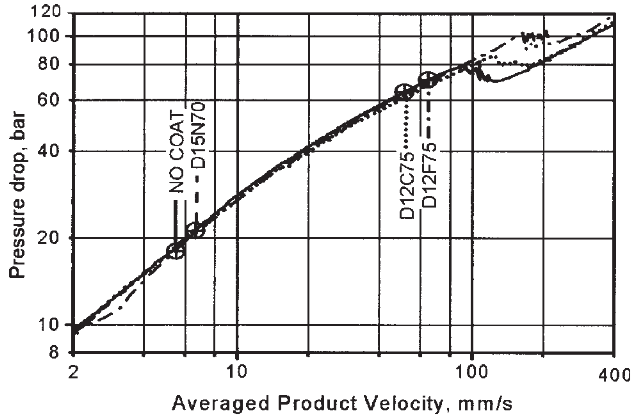

FIG. 4. Characteristic curves for extrusion with the glass die precoated by "Adhesives" (no slip). Onsets of sharkskin are marked by crosses in circles. While the use of these TPUEs does not result in slip, the sharkskin onset is delayed.

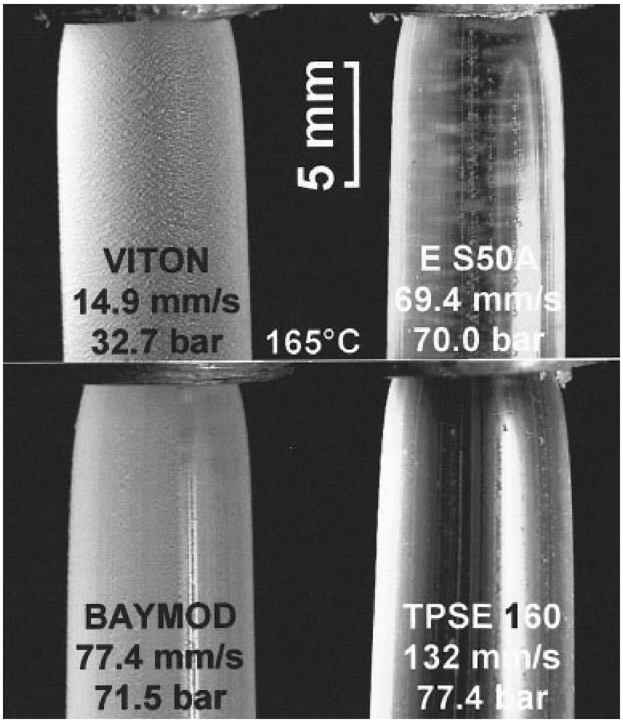

FIG. 5. Extrudate appearances at the onset of sharkskin. A steel die 6 · 32 mm was precoated with PPAs. Extrusion is directed downward.

Choosing TPUE as a processing aid is a challenging task, as there are many combinations of hard and soft segments. We believe that the use of compact linear diisocyanates like methylene diphenyl diisocyanate (MDI) or para-phenylene diisocyanate (PPDI) is preferable for hard segments. For the soft segments (diols), we recommend the use of linear high molecular weight polyesters because of their lower price, good stability under heating, as well as strong adhesion to metals and oxides. For special applications the use of more expensive "Lubricants" could be justified, which are taken either from TPUEs based on polysiloxanes as soft segments or from raw silicone rubbers. The raw silicone rubbers have to be characterized by strong adhesion to metal oxides and curing at processing temperature.

In the processing of PE by extrusion, sharkskin has to be totally eliminated at all surfaces of the product. A thin PPA coating of the die could easily be damaged by sand particles. Quick healing of these scratches is possible if the blend has an excessive amount of PPA with viscosity much lower than that of PE. For example, in blown film experiment the use of 500 ppm of low viscous "Baymod" which is an "Adhe-

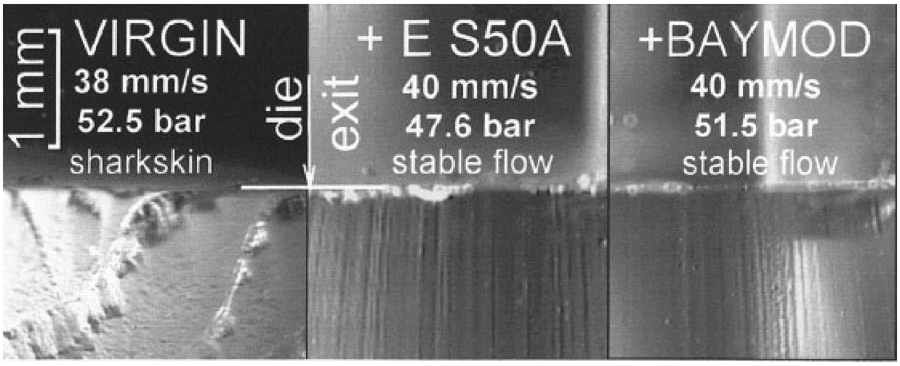

FIG. 6. Extrudate appearances taken at about 40 mm/s at the exit of a glass die 6 · 32 mm. The flow is downward. The die is not coated (left frame), the die is precoated with "E S50A" (middle frame), the die is precoated with "Baymod." "Baymod" do not accumulate at the die face because of its low viscosity opposite "E S50A."

sive" PPA is enough to keep extrusion stable with no visible defects, in comparison to the minutes required to heal scratches with the use of high viscous "E 685A" and "E S50A" from Elastogran even in an amount above 2,000 ppm in the same environment. Very low viscosity of PPA also enhances separation of PPA from PE melt, so that less PPA will be lost through entrapment inside the product and less mass fraction of additives is necessary to stabilize extrusion.

The viscosity at processing temperature mainly depends on molecular weight of the TPUE, while its elasticity in terms of the ratio G1/G2 depends mostly on bonding strength between hard segments, on the length ratio of the hard and soft segments, and flexibility of the soft segments. Both "Lubricant" and "Adhesive" can be of low viscosity in comparison to PE. It is, however, preferable that the melting temperature of the PPA is close to or above the melting temperature of PE, otherwise lubrication of the feed section in a screw extruder lowers mass output of the product. In blown film processing of LLDPE the production rate is limited by the onset of sharkskin instability. With the use of the proposed novel PPAs this instability vanishes. The only remaining problem is an unstable blowing of the bubble. This bubble instability could be delayed by the use of "bimodal" blends of LLDPE and HDPE and by the use of lower processing temperature. Elastic properties of TPUEs depend very much on temperature. In this sense the use of "Adhesives" is more universal, as they do not show a sharp change in elasticity as processing temperature increases. For the given processing temperature, the proper TPUE, which is characterized by low viscosity and by a low ratio of G1/G2 in comparison to the matrix polymer, could be chosen from among many commercially available products.

The origin of sharkskin (melt fracture) in extrusion of LLDPE is still being debated and the mechanism by which TPUEs delay the sharkskin onset is not clear. In accordance with the ideas of Denn and colleagues [7], we believe that sharkskin is a manifestation of periodical failures in adhesion of molten PE to the die exit when the crack of adhesion failure deviates from the die wall and produces a seed crack in the product surface layer. Outside the die the seed cracks develop into a sharkskin structure. From experimental data we see that the "Adhesive" TPUE works as a glue and prevents adhesion failures [8]. It was recently shown that the use of coating from elastic materials at the die surface stabilizes the flow of molten LLDPE. The elastic coating works simultaneously as "Lubricant," i.e., molten polyethylene slips along the coated surface [9]. We think that the coating by "Lubricant" TPUE which is elastic in compari-

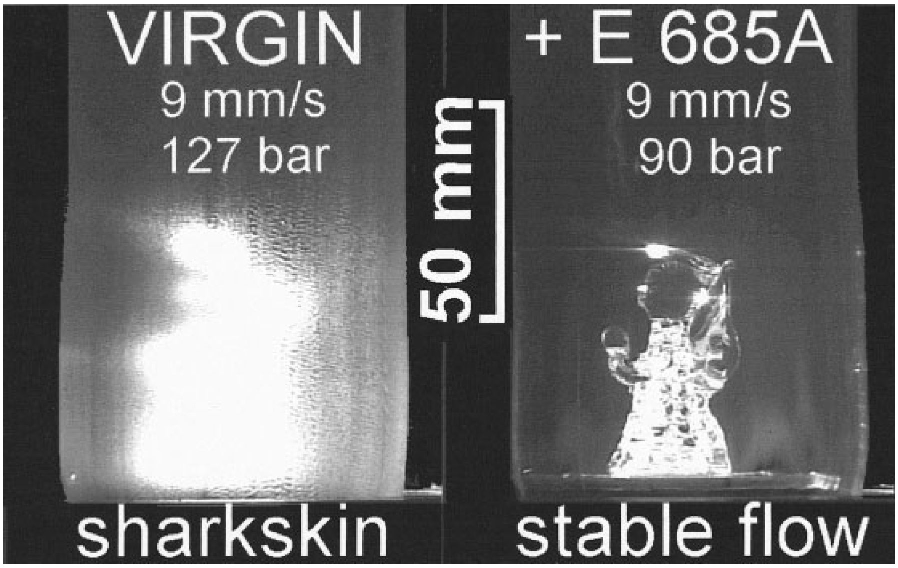

FIG. 7. Appearance of blown film made with a ring die 0.5 · 40 mm. Virgin PE is shown in the left frame, PE is blended with 0.2 wt% of "E 685A" in the right frame. A statuette of an angel stays behind the bubble.

TABLE 1. Onset of sharkskin and step in flow curve for extrusion with the die coated by "Adhesives" and "Lubricants" at 165°C, mechanical properties, and dynamic viscosity of PPAs.

Material of coating	Onset of sharkskin at mm/s	Step in flow curve at mm/s	G1/G2 at 20 Hz	Dynamic viscosity at 0.1 Hz, KPa · s
No coating	M = 5.4	S = 90	K = 1.4	V = 16.8
		Lubricants		
VITON	1.35 · M	0.44 · S	1.3 · K	0.66 · V
ES50A	10.6 · M	1.9 · S	1.4 · K	6.31 · V
E685A	12.0 · M	1.7 · S	1.6 · K	6.13 · V
TPSE80	16.5 · M	2.4 · S	1.7 · K	0.78 · V
D15653	19.8 · M	3.3 · S	2.3 · K	11.5 · V
TPSE160	26.3 · M	2.8 · S	1.8 · K	0.024 · V
TPSE140	25.2 · M	3.0 · S	2.25 · K	2.78 · V
TPSE120	19.1 · M	2.9 · S	2.0 · K	2.15 · V
		Adhesives		
PD15N70	1.2 · M	1.1 · S	0.8 · K	0.75 · V
PD152K	1.8 · M	1.4 · S	0.7 · K	0.13 · V
PD162K	2.0 · M	1.3 · S	0.9 · K	0.20 · V
PD13S	7.3 · M	1.6 · S	0.9 · K	0.67 · V
P45-50/25	8.4 · M	1.7 · S	0.85 · K	0.67 · V
PD12C75	9.4 · M	1.3 · S	0.7 · K	0.07 · V
P45-50/22	10.8 · M	1.6 · S	0.9 · K	0.68 · V
BAYMOD	11.8 · M	1.6 · S	0.85 · K	0.16 · V
P46-73/27	11.9 · M	1.9 · S	0.8 · K	0.53 · V
PD12F75	12.0 · M	1.8 · S	0.7 · K	0.63 · V
ESP9269	12.0 · M	1.8 · S	—	—
P46-73/32	12.8 · M	2.0 · S	0.8 · K	0.41 · V
PD125K	13.4 · M	1.9 · S	0.7 · K	0.06 · V

son to PE keeps the cracks from penetrating into the molten PE. According to Gerde and Marder [10], propagation of shear cracks along the boundary results in slip. After experiments with TPUEs it was always easy to separate solidified PE from metal die. This shows that TPUEs may work as a release agent in injection molding.

CONCLUSIONS

We present here the very first results that demonstrate the potential to lower production costs and to reduce environmental impact by the use of commercially available TPUEs instead of fluorinated polymers. The experiments were performed with LLDPE but the results may contribute to improvement of extrusion, blow molding, and injection molding of other polyolefin resins, copolymers of polyolefins, and blends based on polyolefins. For example, TPUEs could be used as a release agent in injection molding of HDPE. Further experimental and analytical investigations are required to understand the mechanism of TPUEs in slip and suppression of flow instabilities.

The benefits from using TPUE as the PPA include those of the fluorinated PPAs plus a positive impact on printability and adhesion of the product surface to labels and laminating agents. Thus, primary benefits from the use of TPUEs as PPA include:

- Delay of the melt flow instabilities to a higher rate of processing.
- Improved release from metal dies and molds. Reduction in die build-up (die drool).
- Improved printability and adhesion of the final product.
- Lubrication of metal parts, e.g., extrusion dies and molds in the case of "Lubricant" TPUE so that molten PE slips along the surface.

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NOMENCLATURE

FDA	Food and Drug Administration
LLDPE	Linear low density polyethylene
PE	Polyethylene
PPA	Polymer processing aid
TPE	Thermoplastic elastomer
TPUE	Thermoplastic polyurethane-based elastomer

REFERENCES

1. M.M. Denn, *Annu. Rev. Fluid Mech.*, **33**, 265 (2001).
2. A.I. Leonov and A.N. Prokunin, *Nonlinear Phenomena in Flows of Viscoelastic Polymer Fluids*, Chapman & Hall, London, 356 (1994).
3. R.G. Larson, *Rheol. Acta*, **31**, 213 (1992).
4. J.M. Piau and J.F. Agassant, *Rheology for Polymer Melt Processing*, Elsevier, Amsterdam (1996).
5. S. Hatzikiriakos and K. Migler, "Polymer Processing Instabilities: Control and Understanding," Marcel Dekker Series, Vol. 102 (2004).
6. H. Zhou and C. Pozrikidis, *Phys. Fluids*, **6**, 80 (1994).
7. D.A. Hill, T. Hasegava, and M.M. Denn, *J. Rheol.*, **34**, 891 (1990).
8. M. Fujiyama, *J. Appl. Polym. Sci.*, **84**, 2120 (2002).
9. O. Kulikov and K. Hornung, *J. Non-Newtonian Fluid Mech.*, **124**, 103 (2004).
10. E. Gerde and M. Marder, *Nature*, **413**, 285 (2001).