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(54) **PROCEDE POUR LA TRANSFORMATION D'UN POLYMERE THERMOPLASTIQUE**

(54) **THERMOPLASTIC PROCESS**

(57) The present invention relates to a method for processing a thermoplastic polymer which is melt incompatible with polybutylene comprising adding a high melt index polybutylene to the thermoplastic prior to processing.

ABSTRACT

The present invention relates to a method for processing a thermoplastic polymer which is melt incompatible with polybutylene comprising adding a high melt index polybutylene to the thermoplastic prior to processing.

THERMOPLASTIC PROCESS

The present invention relates to a means for extruding or processing a thermoplastic polymer. More particularly, this invention relates to a process for increasing polymer processing rates, by incorporating a high melt index polybutylene into melt incompatible thermoplastic polymers especially polyethylene.

It is well known that some thermoplastics, including thermoplastic elastomers, have excellent properties, but lack good melt processability. Even among readily processable polymers, high toughness and good melt strength are attributes of higher molecular weight grades, and as a result, melt processing machine outputs tend to be inversely related to the toughness required for, e.g. durable goods, and melt strength needed for, e.g. film, thermoforming, blow molding, and injection molding. With the addition of a high melt index polybutylene, polymers which are otherwise difficult to melt process may be processed more easily. Thus, desirable performance properties may be largely retained with little or no sacrifice to melt processability. Therefore, these polymers may be efficiently melt processed while the desirable performance properties of the final product are retained.

Blends of polypropylene and polybutylene have been described, e.g. see U.S. 3,900,534. However the

incorporation of high melt index polybutylene polymers as claimed in the present application has not been disclosed.

The present invention relates to a method for processing a thermoplastic polymer which is substantially melt incompatible with polybutylene, comprising adding a high melt index (or low molecular weight) polybutylene to the thermoplastic polymer prior to processing. For example, if the processing includes an extrusion step, the polybutylene may be added prior to extrusion.

The improved method uses less power and significantly increases polymer throughput without significantly diminishing the properties of the parent polymer. The high melt index polybutylene appears to lubricate the polymer melt and, because it is incompatible with the thermoplastic, continues to operate at the surface of the blend. This novel process may be used to more efficiently recycle waste thermoplastic polymers by allowing a wide diversity of polymer grades to be melt processed with less concern for their melt processability.

The amount of polybutylene added is from 0.2% to 20%, preferably from 1% to 10%, and most preferably 2% to 7% by weight of the resulting mixture and is preferably dry blended with the polymer in powder form, for example prior to extrusion.

The high melt index polybutylene referred to herein is at least one butene-1 polymer containing from 90%,

preferably from 95%, and more preferably from 97%, by weight of isotactic portions. For example, isotactic poly-1-butenes having a low molecular weight, e.g. less than about 280,000 as determined by solution viscosity in "Decalin" (decahydronaphthalene) may be used. Suitable poly-1-butenes have a density of from 0.900 to 0.925, preferably from 0.905 to 0.920 and most preferably from 0.910 to 0.915. Suitable poly-1-butenes have melt indices in the range of from 10 to 1000, more preferably from 20 to 650, and most preferably from 100 to 500, as determined by ASTM D-1238 Condition E, at 190°C. The intrinsic viscosity of the polybutylene may range from 0.03 to 0.20, preferably from 0.06 to 0.11 at 130°C.

A butene-1 polymer (PB) usable herein is either a butene-1 homopolymer or a copolymer or a terpolymer. If a butene-1 copolymer is used, the non-butene comonomer content is preferably from 1 to 30 mole % of either ethylene, propylene, or an alpha olefin having from 5 to 8 carbon atoms. The poly-1-butenes can be modified to increase surface activity by reaction with, for example, maleic anhydride.

Suitable poly-1-butenes can be obtained, for example, in accordance with Ziegler-Natta low-pressure polymerization of butene-1, e.g. by polymerizing butene-1 with catalysts of $TiCl_3$ or $TiCl_3.AlCl_3$ and $Al(C_2H_5)_2Cl$ at temperatures of 10-50°C, preferably 20-40°C, e.g. according

to the process described in DE-A-1,570,353. High melt indices are obtainable by further processing the polymer by peroxide cracking, thermal treatment or irradiation to induce scissons leading to a higher melt flow material.

Duraflex® DP0800, a developmental polybutylene polymer produced by Shell Chemical Company, of Houston, Texas is a particularly suitable polymer. This novel polymer is a homopolymer with a melt index of 200 g/10 min. at 190°C and 490 g/10 min. at 210°C and a molecular weight of 108,000.

Duraflex® PB0400, a commercial polybutylene polymer produced by Shell Chemical Company, is another suitable polymer. The polymer is a homopolymer with a melt index of 20 g/10 min. at 190°C and a molecular weight to 202,000.

The thermoplastics suitable for use in the present invention are any thermoplastics which are incompatible in the melt with polybutylene.

Melt incompatible thermoplastic polymers which can be processed using the present method include a broad range of melt incompatible thermoplastics and thermoplastic elastomers. These thermoplastics include but are not limited to low melt index polyethylene including high density polyethylene, low density polyethylene, linear low density polyethylene and other polyethylene copolymers.

Other thermoplastics include polyamides (nylons),

polyesters, polycarbonates, poly-4-methyl pentene, polyimides, polysulfones, polyketones, polyphenylene oxide, ethylene vinyl alcohol, polyvinyl chloride, polyacetals, polystyrene, and similar polymers and copolymers.

Melt incompatible thermoplastic elastomers include styrenic block copolymers, polyesters, polyolefins, and polyurethanes.

Uncured thermosetting materials may be used in the present invention and many include epoxides, crosslinkable polyesters, thermoset polyurethanes, cyanoacrylates, phenolics, urea formaldehydes, and silicones.

Thermoplastic polymers usable herein can be either homopolymers or copolymers. If copolymers are used, they can be random or block copolymers. For example, a suitable thermoplastic polymer is a polyolefin homopolymer or a polyolefin copolymer comprising from 1 to 30 mole% of an alpha-olefin having from 2 to 8 carbon atoms. Suitable thermoplastic polymers preferably have a melt index of less than 60, preferably less than 20, more preferably less than 15, and most preferably less than 10, as measured by ASTM D-1238, Condition L at 230°C.

A preferred method uses 5% by weight of a high melt index butene-1 homopolymer having a melt index equal to or greater than 20, and 95% by weight of a thermoplastic, e.g. a linear low density polyethylene.

Blending of the components can occur by, for

example, dry tumble blending, masterbatch, or melt compounding techniques. The method of combining the ingredients of the formulation is important. For example, in most cases, it is desirable to use the least amount of energy to merge the components into an effective blend. Therefore the preferred method of blending is dry blending the components in a powder form.

EXAMPLES

Blends were prepared with GRSN-7047 linear low density polyethylene (LLDPE) with a 1.0 melt index available from Union Carbide Corporation, Duraflex® DP0800, polybutylene and Duraflex® PB0400 polybutylene, available from Shell Chemical Company, Houston, Texas. The components were dry blended before extruding.

The typical physical properties of the high index polybutylene (DP0800) are listed below.

TABLE I

Typical Physical Properties of DP0800 Polybutylene

	ASTM	Polybutylene DP0800 Units	
	Test Method	Metric	English
Melt Index @ 190°C	D1238 "E"	200g/10min	-
@ 230°C	D1238 "L"	490g/10min	-
Density	D1505	0.915g/cm^3	57.1 lb/ft
Tensile strength @ yield	D638	13.8 MPa	2000 psi
Tensile strength @ break	D638	29.0 MPa	4200 psi
Elongation at break	D638	350%	-
Modulus of elasticity	D638	241 MPa	35000 psi
Hardness, Shore	D2240	55 D Scale	-
Brittleness temperature	D746	-18°C	0°F
Melting point range	DSC	124-126°C	225-259°F
Soft point, Vicat	D1525	116°C	241°F
Thermal conductivity, at 25°C (77°F)	C177	16Kcal/m^2/hr/°C/cm	1.25Btu/ft^2/hr/°F/in

In Tables II to V the blends were extruded using a 3.18 cm (1¼") Brabender extruder with temperatures at Zone 1 of 190°C and at Zones 2-5 of 215°C and a L/D of 24:1.

In Table VI the blends and control were extruded using a 1.91 cm (3/4 inch) Brabender extruder with temperatures at Zones 1-4, 175°C and 234°C at the die. The L/D was 25:1. The results are recorded in Tables II to V below.

It can be seen from the data that significant improvements in throughput and power required are achieved using the claimed process.

Polybutylene with a melt index as low as 20 g/10 min. and concentrations as low as 1.0w% showed improvements in processability.

TABLE II

30 RPM Extrusion Conditions for LLDPE + DP0800

	BACK PRESSURE		CURRENT	THROUGHPUT	
	MPa	(psi)	AMP	kg/hr	(lbs/hr)
Control	7.929	(1150)	6.75	3.60	(7.93)
2.5w% PB	6.72	(975)	5.25	3.03	(6.68)
5.0w% PB	6.55	(950)	5.0	3.0	(6.7)

TABLE III

60 RPM Extrusion Conditions for LLDPE + DP0800

	BACK PRESSURE		CURRENT	THROUGHPUT	
	MPa	(psi)	AMP	kg/hr	(lbs/hr)
Control	10.51	(1525)	8.5	7.158	(15.78)
1.0w% PB	9.480	(1375)	7.25	6.319	(13.93)
2.5w% PB	8.791	(1275)	6.75	5.620	(12.39)
5.0w% PB	7.929	(1150)	6.25	5.529	(12.19)

TABLE IV

90 RPM Extrusion Conditions for LLDPE + DP0800

	BACK PRESSURE		CURRENT	THROUGHPUT	
	MPa	(psi)	(amps)	kg/hr	(lbs/hr)
Control	11.79	(1710)	7.5	11.1	(24.4)
2.5w% PB	9.825	(1425)	6.25	8.550	(18.85)
5.0w% PB	9.136	(1325)	6.25	8.110	(17.88)

TABLE V

60 RPM Extrusion Conditions for LLDPE + PB0400

	BACK PRESSURE		CURRENT	THROUGHPUT	
	MPa	(psi)	(amps)	kg/hr	(lbs/hr)
Control	10.51	(1525)	8.5	7.158	(15.78)
2.5w%	9.584	(1390)	7.5	6.146	(13.55)

Control = 100% LLDPE

TABLE VI

Throughput Enhancement of LLDPE by DP0800

		MELT TEMP (°C)	RPM	BACK PRESSURE MPa	(psi)	THROUGHPUT (g/2 min)
5	Control	234	100	10.0	(1450)	85.9
	Control	234	100	10.0	(1450)	84.3
	Control	230	175	12.1-12.8*	(1750-1850*)	141.9*
	5.0 w% PB	234	100	5.2	(750)	74.7
10	5.0 w% PB	235	175	8.62	(1250)	120.0
	2.0 w% PB	235	174	10.0	(1450)	131.4

*Extrudate was discolored and severely degraded

In Table VI the back pressure was raised by increasing the RPM for the blends containing PB to levels approaching the control back pressure. Polymer throughput was significantly increased as can be seen in the last two runs containing PB with extruder speed at 175 and 174 RPM.

Although the invention has been described with preferred embodiments it is to be understood that modifications and variations may be made without departing from the spirit and scope of this invention as claimed.

The embodiments of the invention, in which an exclusive privilege or property is claimed, are defined as follows:

1. A method for processing a thermoplastic polymer which is substantially melt incompatible with polybutylene, comprising adding a high melt index polybutylene to the thermoplastic polymer prior to processing.

2. A method according to claim 1, including an extrusion step, wherein the polybutylene is added prior to extrusion.

3. A method according to claim 1 or 2 wherein the thermoplastic polymer is a polyolefin homopolymer or a polyolefin copolymer comprising from 1 to 30 mole% of an alpha-olefin having from 2 to 8 carbon atoms.

4. A method according to claim 1 or 2 wherein the thermoplastic polymer is a low melt index polyethylene homopolymer or copolymer.

5. A method according to claim 1 or 2 wherein the thermoplastic polymer is high density polyethylene, low density polyethylene or linear low density polyethylene.

6. A method according to claim 1 or 2 wherein the thermoplastic polymer is a thermoplastic elastomer.

7. A method according to claim 1 or 2 wherein the thermoplastic polymer is an uncured thermosetting polymer.

8. A method according to claim 1 or 3 wherein the thermoplastic polymer has a melt index of less than 20, as

measured by ASTM D-1238, Condition L at 230°C.

9. A method according to claim 1 or 3 wherein the thermoplastic polymer has a melt index of less than 10.

10. A method according to claim 1 or 2 wherein the polybutylene has a melt index of from 10 to 1000, as determined by ASTM D-1238 Condition E, at 190°C.

11. A method according to claim 1 or 2 wherein the polybutylene has a melt index of from 20 to 650.

12. A method according to claim 1 or 2 wherein the polybutylene has a melt index of from 100 to 500.

13. A method according to claim 1 or 2 wherein the amount of polybutylene added is from 0.2% to 20% by weight of the resulting mixture.

14. A method according to claim 1 or 2 wherein the amount of polybutylene is from 1% to 10% by weight of the resulting mixture.

15. A method according to claim 1 or 2 wherein the amount of polybutylene is from 2% to 7% by weight of the resulting mixture.

16. A method according to claim 1 or 2 wherein the polybutylene is a butene-1 homopolymer or a butene-1 copolymer comprising from 1 to 30 mole% of an alpha-olefin having from 2 to 8 carbon atoms.

17. A method according to claim 1 or 2 comprising the additional step of shaping the thermoplastic polymer.