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(54) Title: CARBON MONOXIDE INTERPOLYMERS STABILIZED AGAINST VISCOSITY CHANGES WITH HINDERED PHENOLS

(57) Abstract

A process is described for stabilizing the melt flow rate and melt tension of ethylene-carbon monoxide interpolymers with a hindered phenol antioxidant. The antioxidant is melt blended with the polymer before it is exposed to air.

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CARBON MONOXIDE INTERPOLYMERS STABILIZED AGAINST VISCOSITY CHANGES WITH HINDERED PHENOLS

This invention relates to a process for stabilizing the melt flow rate and melt tension of ethylene-carbon monoxide interpolymers with a hindered phenolic antioxidant. The antioxidant is melt blended with the polymer before the polymer is exposed to air.

Ethylene-carbon monoxide interpolymers (ECO) are a known class of compounds which are typically prepared by high pressure, free-radical initiated polymerization reactions. The polymerization reaction can also be catalyzed with coordination catalysts.

The ECO polymers are known to have poor resistance to thermal degradation during post-polymerization processing. Viscosity changes have even been observed during storage under warehouse conditions. The changes in melt flow rate and melt tension can render the ECO polymers unacceptable for subsequent processing and use. The stability problems are particularly severe for ECO polymers having a high carbon monoxide content (e.g., 10 mole percent).

Summary of the Invention

Viscosity-stabilized ECO polymers are obtained by a process which comprises intimately melt-blending the ECO interpolymer with a hindered phenolic antioxidant prior to exposing the interpolymer to air. The hindered phenol is added in an amount effective to stabilize the ECO polymer blend against viscosity changes. The resulting blend has a stable melt flow rate and melt tension under ambient conditions of transportation and storage and under conditions of use in melt processing operations.

Any of the known class of ECO interpolymers, or mixtures thereof can be used in the present invention.

In a conventional ethylene-carbon monoxide (ECO) polymerization, ethylene, carbon monoxide and a free-radical initiator are charged to a high pressure polymerization reactor and maintained at suitable temperature and pressure to interpolymerize the ethylene and carbon monoxide. Reactor pressures are typically maintained at from 70 MPa (10,000 psi) to 350 MPa (50,000 psi), preferably from 100 (14,500 psi) MPa to 200 (29,000 psi) MPa, and reactor temperature at from 50°C to 300°C, preferably from 100°C to 250°C. The reactor can be of any suitable type, such as, for example stirred autoclave, tubular, batch, continuous, etc. The free-radical initiator can be oxygen; an organic peroxide (e.g., t-butyl peroctoate, benzol peroxide, lauryl peroxide, t-butyl peroxypivalate, di-t-butyl peroxide, di(2-ethylhexyl) peroxy dicarbonate, and t-butyl peracetate); or an azo compound (3.g., azobis(1-cyano-1,4-dimethylbutane), and azobisisobutyronitrile). The initiator is preferably an azo compound, although

the invention is not restricted to the choice of initiator.

As is known in the art, an inert organic solvent may be employed to transfer optional monomers and/or initiator into the reactor. Especially where relatively small proportions of these components make accurate metering difficult, employment of a solvent is preferred. Such solvents generally include, for example, methylethylketone and isooctane. It is also known to employ a chain transfer agent such as, for example, isobutane, to control the average molecular weight of the interpolymer within selected ranges.

Generally, the ECO interpolymer is recovered from the reactor by means of a letdown valve and a series of separators. Typically, a high pressure separator receives the interpolymer and unreacted monomer directly from the reactor. The high pressure separator is generally operated at a pressure of from 15 (2000 psi) MPa to 24 (3500 psi) MPa. A low pressure separator receives the interpolymer and residual unreacted monomer from the high pressure separator. The low pressure separator is typically operated at a pressure of from 0 kPa to 500 kPa (gauge). The ECO interpolymer is then discharged from the low pressure separator into a feed port of a primary extruder (which may be equipped with a devolatilization zone(s) for residual monomer removal) operating at a temperature above the melting point of the polymer. The extrudate is then typically pelletized using conventional equipment, such as, for example, an underwater pelletizer. The pelletized ECO interpolymer is typically air dried and subsequently stored for shipment and use. It is common for the ECO inter-polymers to be

formulated with various additives by dry blending and/or melt blending the pelletized ECO with the additives in conventional equipment, such as, for example, Brabenders and roll mills.

Free-radical initiated polymers can generally be distinguished from coordination catalyzed polymers in that the former are generally branched, whereas the coordination catalyzed polymers tend to be less branched and more linear. The present invention is particularly applicable to stabilizing free-radical initiated ECO polymers having a relatively high CO content, e.g. above 5 percent by weight. Viscosity stability is less of a problem in ECO polymers containing lower levels of CO, so the benefits derived from the addition of stabilizers to such polymers are not as pronounced as the stabilization observed in ECO polymers having high CO content, e.g. above 10 percent by weight. There does not appear to be any upper limit on the CO content of ECO which may be effectively stabilized in accordance with the present invention, although as a practical matter, ECO polymers containing more than 35 percent by weight CO are difficult to prepare commercially. Thus, the ECO polymers preferably have a CO content of from 5 to 35 percent by weight; more preferably, from 10 to 35 percent by weight; and ECO polymers having a CO content of from 15 to 35 percent by weight are especially preferred for use in the present invention.

The ECO polymer blends produced by this process have a melt flow rate from 0.1 to 300 dg/min, preferably from 1 to 100 dg/min. As used herein, melt flow rate (MFR) is determined in accordance with ASTM D-1238, Condition E (190°C/2.16 kg). The ECO polymer blends generally have a melt tension less than 8, preferably

less than 6. As used herein, melt tension (MT) is measured as an extrudate from a Tinius-Olsen Extrusion Plastometer model MP987 over a range of 30-3000 rpm at I_2 conditions of 190°C and 2.16 kg weight.

The ECO interpolymers of the present invention can include a minor proportion of another monomer in the polymer chain. Suitable termonomers include, for example, C_3-C_8 aliphatic olefins (e.g., propylene, butene-1, hexane-1, and octane-1) and/or ethylenically unsaturated organic acids having 3 to 8 carbon atoms (e.g., acrylic acid, methacrylic acid, and 1-butenoic acid); and alkyl esters or metal salts of these acids (e.g., ethyl acrylate, methyl methacrylate, 2-ethylhexyl acrylate, sodium acrylate, and potassium methacrylate). Hydrogenated ECO polymers contain -CH(OH)- groups along the polymer chain. Hydrogenated ECO polymers, such as those disclosed in U.S. 2,495,292, are also suitable polymers for use in the present invention.

The hindered phenolic antioxidants used in the present invention form a known class of compounds which includes, for example, tetrakis(methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate)methane; 2,6-di-t-butyl-p-cresol; 2-t-butyl-4-hydroxyanisole; 3-t-butyl-4-hydroxyanisole; and 2,6-di-t-butyl-4-sec-butylphenol. Tetrakis(methylene-3-(3,5-di-t-butyl-5-hydroxy-phenyl)propionate)methane is especially preferred.

The hindered phenolic antioxidant should be in intimate admixture with the ECO polymer such that it is distributed substantially uniformly throughout the polymer composition. Thus, the hindered phenolic antioxidant is generally added to the ECO polymer in a

readily dispersible form, such as, for example, in a finely divided state or dissolved in a solvent.

In preparing the composition of the invention, the hindered phenolic antioxidant is added to the ECO polymers in an amount effective to impart viscosity-stability. Concentrations below 500 ppm are generally not sufficiently effective. Generally, no additional stabilization is observed at concentrations above 5000 ppm, and other properties of the ECO can be adversely affected at such higher concentrations. Thus, it is preferred to use at least 500 ppm of the scavenger, and more preferably from 1000 to 5000 ppm.

The hindered phenolic antioxidant and the ECO polymer are intimately mixed under conditions at which the ECO is molten. It is essential that the hindered phenolic antioxidant is added to and mixed with the ECO polymers prior to exposing the ECO polymer to air. It has been found, quite surprisingly, that ECO polymers stabilized according to this procedure have enhanced viscosity stabilization over "equivalent" polymer blends formed by (1) dry blending the hindered phenolic antioxidant with pelletized ECO, or (4) melt blending the hindered phenolic antioxidant with an ECO polymer which has been exposed to air more than one or two hours following production.

The hindered phenolic antioxidant may be added to the ECO polymers at any convenient point downstream of the copolymerization reactor vessel but prior to exposing the ECO polymer to air. Typical equipment downstream of the reactor includes separators in which the unreacted monomers and ethylene are removed from the molten ECO, primary extruders, and finishing extruders.

Mixing is generally accomplished by the shear imparted to the blend as it passes through the processing equipment. Other mixing equipment which may be suitably employed includes compounding extruders, Banbury mixing extruders, intensive mixing or multi-screw extruders, roll mills or the like.

The invention is illustrated by way of the following examples:

Examples 1-3 and Comparative Example A

In the following examples and comparative example, ECO interpolymers having 10 weight percent CO content were produced in a conventional high pressure autoclave reactor and discharged into a high pressure separator, a low pressure separator, and then into the feed port, of a primary extruder and pelletized. Examples 1-3 had varying concentration of IRGANOX 1010 added to the polymer either in the low pressure separator (LPS) (Example 1) or in the high pressure separator (HPS) (Examples 2-3) while Comparative Example A had no antioxidant added. Additive concentrations and initial MFR and MT data presented in Table IV below.

TABLE I

Example	Comp. A	1	2	3
IRGANOX 1010 (ppm)	0	1400	612	656
Initial MFR (dg/min)	10.1	10	10	10
Initial MT (g)	3.38	3.45	2.65	2.85

The pelletized resins were stored under ambient conditions in a polyethylene bag and their melt tension (MT) were monitored following production. The test results were shown in Table II below.

TABLE II

Time Since Production (hours)	MT (g)			
	Comp. A (0 ppm)	Example 1 (1400 ppm)	Example 2 (612 ppm)	Example 3 (656 ppm)
0	3.41	3.5	2.65	2.85
1	5.3	3.7	2.90	2.90
2	4.5	3.8	3.05	3.5
4	--	--	3.1	3.72
8	--	--	3.35	3.75
10	4.3	3.6	--	--
12	--	--	3.55	3.7
14	--	3.4	--	--
22	4.8	--	--	--
24	4.4	--	3.8	3.0
26	--	--	--	--
48	4.4	--	3.55	3.7
50	--	--	--	--
72	5.6	--	3.8	3.78
74	--	3.7	--	--
97	3.8	4.5	--	--
121	6.0	4.2	--	--
144	7.3	--	4.0	3.73
145	--	3.7	--	--
192	8.0	--	3.35	4.3
216	--	--	3.5	3.68
240	--	--	4.1	3.62
241	--	4.1	--	--
265	CNA	3.7	--	--
289	CNA	--	--	--
313	CNA	--	--	--

-- = Not analyzed.

CNA = Too high to measure

Example 1 was similar in every request to Comparative Example A except that 1400 ppm IRGANOX 1010 were added to the LPS. The viscosity as represented by MT, of the Comparative Example A increased unacceptably under ambient temperature storage while the polymer in examples 1, 2 and 3 were substantially viscosity stable.

The viscosity increase in Comparative Example A rendered the ECO unacceptable for subsequent processing and use where consistent performance was required. By contrast, the viscosity (MT) of Example 1 had not changed even after 265 hours in storage.

Examples 4-6 and Comparative Examples B-D

Additional ECO interpolymers (10 weight percent CO, 10 MFR) were prepared and MT monitoring were performed as described above that the samples were made in another high pressure autoclave reactor and the hindered phenolic antioxidant, IRGANOX 1010, additive were only injected into the HPS.

Results in Table III below show significant increases in MT for the resins in Comparative Examples B, C and D without IRGANOX 1010. After 260 hours of storage at ambient conditions the MT of Comparative Examples B, C and D could not be measured. However, Examples 4-6, prepared with 780, 704 and 1050 ppm IRGANOX 1010 added to the HPS, demonstrated excellent viscosity stabilization over time.

TABLE III

Time Since Production (hours)	MT (g)					
	Comp. B (0 ppm)	Comp. C (0 ppm)	Comp. D (0 ppm)	Ex. 4 (780 ppm)	Ex. 5 (704 ppm)	Ex. 6 (1050 ppm)
0	3.9	4.7	4.5	4.5	2.3	2.4
216	7.9	CNA	9.8	4.5	2.6	2.2
360	CNA	CNA	CNA	6.0	3.0	2.4

Having described the invention above, many variations in the materials, proportions and method of preparation, as well as in the illustrated details of the improvement, will occur to those skilled in the art. It was intended that all such variations which fall within the scope and spirit of the appended claims be embraced thereby.

1. In a method for preparing an ethylene-carbon monoxide interpolymer, comprising polymerizing a monomer mixture containing ethylene and carbon monoxide in the presence of a free-radical polymerization initiator in a copolymerization reactor vessel, and recovering an ethylene-carbon monoxide (ECO) interpolymer containing at least 10 up to 35 percent by weight carbon monoxide in interpolymerized form, the improvement characterized by intimately melt-blending the ECO interpolymer with from 500 to 5000 ppm of a hindered phenol antioxidant at any convenient point downstream of the copolymerization reaction vessel, but prior to exposure to air.

2. The method of Claim 1, wherein said hindered phenol is tetrakis(methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate)methane, 2,6-di-t-butyl-p-cresol, 2-t-butyl-4-hydroxyanisole, 3-t-butyl-4-hydroxyanisole, or 2,6-di-t-butyl-4-sec-butylphenol.

3. The method of Claim 2, wherein said hindered phenol is tetrakis(methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate)methane.

4. The method of Claim 1, wherein said hindered phenol is added in an amount of from 1000 to 5000 ppm of the resulting blend.

5. The method of Claim 1, wherein said hindered phenol is added to said interpolymer in a separator or primary extruder downstream of a polymerization reactor.

6. The product produced by the method of any of Claims 1 through 5 characterized by improved stability against viscosity changes.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/03950

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08K5/13; C08L73/00; C08J3/20

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08K ; C08L ; C08J ; C08G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	US,A,3 929 727 (DONALD H. RUSSELL) 30 December 1975 see column 2, line 36 - line 44 see claims 1-3	1,4,6
Y	EP,A,0 326 223 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 2 August 1989 see page 2, line 41 - page 3, line 12 see claims 1-22	1,4,6

° Special categories of cited documents :[10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9203950 SA 60573

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-3929727	30-12-75	None		
EP-A-0326223	02-08-89	AU-A-	2878889	03-08-89
		JP-A-	1279962	10-11-89
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