

Certain ethylene-propylene polymers and certain styrene-butadiene polymers are well known elastomers which are commercially available from a variety of sources.

If the olefin polymer is an ethylene polymer, the molar ethylene content is preferably in the range of 20 to 80 percent, and more preferably 30 to 70 percent. When propylene and/or butene-1 are employed as comonomer(s) with ethylene, the ethylene content of such copolymers is most preferably 45 to 65 percent, although higher or lower ethylene contents may be present. Most preferably, the polymers used in this invention are substantially free of ethylene homopolymer and exhibit a degree of crystallinity such that, when functionalized, they are readily soluble in mineral oils.

The polymers employed in this invention generally possess a number average molecular weight of at least greater than 50,000, preferably at least 100,000, more preferably at least 150,000, and most preferably at least 200,000. Generally, the polymers should not exceed a number average molecular weight of 500,000, preferably 400,000, and more preferably 300,000. The number average molecular weight for such polymers can be determined by several known techniques. A convenient method for such determination is by size exclusion chromatography (also known as gel permeation chromatography (GPC)) which additionally provides molecular weight distribution information, see W. W. Yau, J. J. Kirkland and D. D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

A measurement which is complementary to a polymer's molecular weight is the melt index (ASTM D-1238). Polymers of high melt index generally have low molecular weight, and vice versa. The grafted polymers of the present invention preferably have a melt index of up to 20 dg/min, more preferably 0.1 to 10 dg/min.

The polymers employed in this invention may generally be prepared substantially in accordance with procedures which are well known in the art. The polymers for use in the present invention can thus be prepared by polymerizing monomer mixtures comprising olefins such as alpha-olefins having from 3 to 20 carbon atoms, including monoolefins such as propylene, 1-butene, 2-butene, isobutene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 2-pentene, propylene tetramer, diisobutylene, and triisobutylene; diolefins such as 1,3-butadiene, 1,2-pentadiene, 1,3-pentadiene, isoprene, 1,5-hexadiene, 2-chloro-1,3 butadiene, aromatic olefins such as styrene, alpha-methyl styrene, ortho-methyl styrene, meta-methyl styrene, para-methyl styrene, and para-t-butyl styrene; (and mixtures thereof) in the presence of a catalyst system, described below. The co-monomer content can be controlled through the selection of the catalyst component and by controlling the partial pressure of the various monomers. The resulting polymers can be poly-alpha-olefins including random copolymers, block copolymers, and random block copolymers.

The catalysts employed in the production of the reactant polymers are likewise well known. One broad class of catalysts, particularly suitable for polymerization of alpha-olefins,

is generally known as coordination catalysts or Ziegler-Natta catalysts, and comprises a metal atom with certain complexing ligands.

Polymerization using coordination catalysis is generally conducted at temperatures ranging between 20°C and 300°C, preferably between 30°C and 200°C. Reaction time is not critical and may vary from several hours or more to several minutes or less, depending upon factors such as reaction temperature, the monomers to be copolymerized, and the like. One of ordinary skill in the art may readily obtain the optimum reaction time for a given set of reaction parameters by routine experimentation. Preferably, the polymerization will be completed at a pressure of 1 to 300 MPa (10 to 3,000 bar), and generally at a pressure within the range of 4 to 200 MPa (40 to 2,000 bar), and most preferably, the polymerization will be completed at a pressure within the range of 5 to 150 MPa (50 to 1,500 bar).

After polymerization and, optionally, deactivation of the catalyst (e.g., by conventional techniques such as contacting the polymerization reaction medium with water or an alcohol, such as methanol, propanol, isopropanol, etc., or cooling or flashing the medium to terminate the polymerization reaction), the product polymer can be recovered by processes well known in the art. Any excess reactants may be flashed off from the polymer.

Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g., C1 to C4 alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, methyl fumarate, etc. Maleic acid and its derivatives are particularly suitable.

Typically, 0.01 to 50g of said monounsaturated carboxylic reactant are charged to the reactor per kg of polymer charged; more commonly the amount would be 0.1 to 5g.

Not all of the polymer will necessarily react with the monounsaturated carboxylic reactant, in which case the reaction mixture will contain unreacted polymer. The unreacted polymer is typically not removed from the reaction mixture, but the product mixture, stripped of any monounsaturated carboxylic reactant, is employed as described hereinafter. Characterization of the average number of moles of monounsaturated carboxylic reactant which have reacted per mole of polymer charged to the reaction (whether it has undergone reaction or not) is based upon (i) determination of the saponification number of the resulting product mixture using potassium hydroxide; and (ii) the number average molecular weight of the polymer charged, using techniques well known in the art. This characterization is defined with reference to the resulting product mixture. The term "polyolefin having grafted acid functionality" is intended to refer to the product mixture whether or not it contains any unreacted polymer chains.

Accordingly, the amount of carboxylic acid functionality on the grafted polyolefin will normally be 0.001 to 5 weight percent, by which it is meant that -COOH groups will comprise this weight percent of the grafted polyolefin. It is preferred that the amount of carboxylic acid functionality will be 0.01 to 2 weight percent, and more preferably 0.1 to 1 weight percent.

The monounsaturated carboxylic reactant can be reacted with (grafted to) the polyolefin by a variety of methods. For example, the polymer can be first halo-

Example 5. Preparation of Grease.

To a large Hobart™ mixer is charged 2400g of 800 SUS lubricating oil, 268g 12-hydroxy stearic acid, 10g naphthenic acid, 2g antifoam agent from Dow Corning, and 368g of a 10% solution of LZ®7060 hydrocarbon copolymer rubber, functionalized in solution process with maleic anhydride to a total acid number (for the polymer) of 10. The mixture is heated to 80°C.

In a separate container, 44g LiOH·H₂O, 160g water, and 1.6g calcium hydroxide are charged and heated to 80°C with stirring.

The two mixtures are combined and slowly heated to 100°C. Water is continuously removed over 1.5 hours. After removal is complete the mixture is heated to 198°C over 45 minutes and held at temperature for an additional 30 minutes. Heating is discontinued and the reaction is allowed to cool to 170°C over 15 minutes. The pH of the mixture is measured to confirm proper incorporation of the base (found: 10.2. expected: 10-11). To the reaction mixture is added 906.5g additional 800 SUS mineral oil over 5 minutes. The mixture is cooled to 80°C.

The mixture is milled on a Sonic Trihomo™ mill for 1 pass. The resulting material is a grease which has the following physical characteristics:

Penetration (ASTM D-217):

0 stroke: 264

60 stroke: 253

10,000 stroke: 248

Water spray off (ASTM D-4049): 13.5%

Dropping point (ASTM D-2265): 180°C

Example 6. Preparation of Grease.

Example 5 is substantially repeated except that the functionalized polymer has a total acid number of 30. The final addition of 800 SUS mineral oil is 910.5g. The grease which is prepared has the following properties:

Penetration (ASTM D-217):

0 stroke: 303

60 stroke: 300