

GRINDING OF LIQUID CRYSTALLINE POLYMERS

FIELD OF THE INVENTION

5 Thermotropic liquid crystalline polymers are readily ground to smaller particle sizes by using a two or more stage grinding process.

TECHNICAL BACKGROUND

10 Thermoplastic polymers which are in fine particle form are often desired for uses such as papermaking and making nonwoven cloth and other structures. Most polymers can be ground by conventional methods, although some polymers are ground most readily if they are cooled, for example to dry ice or liquid nitrogen temperatures.

15 Thermotropic liquid crystalline polymers (LCPs) are more difficult to grind to small particles because of their inherently fibrous nature. Such LCPs usually have oriented domains in the solid state, and when such domains are broken up they form smaller domains (particles) which

20 are also oriented. No matter how much these domains are broken up they retain their orientation, and eventually come to resemble short stiff fibers, although these fibrous materials do not necessarily have round cross sections.

25 As these fibrous materials are formed, for example from pellets of LCP, they tend to form clumps which other hinder the grinding action of the apparatus which is breaking up the LCP particles. Although breakdown of the LCPs will still take place, the process becomes very slow

30 and inefficient, see for instance U.S. Patent 5,100,605. It has now been found that two or more stage grinding processes are much more efficient in reducing LCPs to relatively small particles.

U.S. Patent 5,100,605 describes the grinding of a (largely) isotropic LCP formed by extruding the LCP at or near its so-called clearing temperature (temperature above which it is no longer liquid crystalline). In an example a two stage grinding process is described. The present invention concerns grinding LCPs with are anisotropic.

U.S. Patent 6,174,405 describes grinding of low molecular weight LCP (essentially "prepolymers") to powders. No mention is made of a two stage grinding process.

U.S. Patent 5,922,453 and Japanese Patent Application 8-13245 describe the grinding of LCPs to smaller particle materials. No mention is made of multistage grinding processes in these references.

SUMMARY OF THE INVENTION

This invention concerns, a process for grinding an anisotropic thermotropic liquid crystalline polymer to form small particles of said anisotropic thermotropic liquid crystalline polymer from larger particles of said anisotropic thermotropic liquid crystalline polymer, wherein the improvement comprises, grinding said anisotropic thermotropic liquid crystalline polymer in two or more separate stages.

This invention also concerns, a process for forming small particles from larger particles of an anisotropic thermotropic liquid crystalline polymer, comprising:

- (a) grinding said anisotropic thermotropic liquid crystalline polymer in a first grinding apparatus;
- (b) removing said anisotropic thermotropic liquid crystalline polymer from said first grinding apparatus;
- (c) grinding said anisotropic thermotropic liquid crystalline polymer from (b) in a second grinding apparatus; and

(d) removing said anisotropic thermotropic liquid crystalline polymer from said second grinding apparatus.

DETAILS OF THE INVENTION

5 Herein certain terms are used, and some of them are:

 By a "grinding apparatus" is meant any apparatus which can exert enough shearing and/or crushing force to cause the material being ground (usually an LCP) to be broken into smaller pieces. Such apparatuses includes
10 hammermills including disintegrators and pin mills, disc mills, fluidized bed air-jet mills, jaw crushers, gyratory crushers, cage mills, pan crushers, ball, pebble rod and tube mills, disk attrition mills, attritors, disc refiners, etc.

15 By "LCP" is meant a polymer which is anisotropic when tested by the TOT test as described in U.S. Patent No. 4,118,372, which is hereby incorporated by reference. By thermotropic is meant the LCP may be melted and is anisotropic in the melt, as described in the TOT test.
20 Herein "LCP" includes blends of LCPs with other polymers, so long as the LCP is at least about 50 weight percent of the polymer blend, based on the total amount of polymer in the blend.

 By "anisotropic" herein is meant that the LCP in the
25 solid form (to be ground) is oriented. This may be tested by grinding the LCP particles. If the LCP is anisotropic, when small enough particles are produced they will be fibrous, that is short and fiber-like (although usually stiff) in nature. Preferably the LCP does not
30 have a clearing temperature, that is it decomposes at a temperature before reaching a clearing temperature.

 By "grinding" herein is meant reducing solid particles in size using a grinding apparatus (see above).

By "a" or "an" herein, such as when referring to an LCP, is meant one or more.

By "comprising" herein is meant the named items (materials), and any other additional materials or compositions may be present.

By "classified" herein is meant that the ground (at any stage) LCP is separated into classes of particle sizes. These may be a range of sizes, such as 30 to 60 mesh (passing through a 30 mesh screen but retained by a 60 mesh screen), or larger (retained by a 30 mesh screen) or smaller than 30 mesh (passing through a 30 mesh screen). Unless otherwise indicated sieve sizes herein are slotted screens with slots about 1.0 cm long and whose width is equivalent to the opening in a US standard screen of the same nominal mesh size. Preferably after the last grinding stage a majority of the LCP will pass through a 30 mesh screen, more preferably a 60 mesh screen.

By a grinding stage (or step) herein is meant placing the LCP to be ground into a grinding apparatus, reducing the average (mean or median) particle size of the LCP, and removing the LCP from the grinding apparatus.

Herein an LCP is ground. Useful LCPs include those which are described in U.S. Patent Nos. 3,991,013, 3,991,014 4,011,199, 4,048,148, 4,075,262, 4,083,829, 4,118,372, 4,122,070, 4,130,545, 4,153,779, 4,159,365, 4,161,470, 4,169,933, 4,184,996, 4,189,549, 4,219,461, 4,232,143, 4,232,144, 4,245,082, 4,256,624, 4,269,965, 4,272,625, 4,370,466, 4,383,105, 4,447,592, 4,522,974, 4,617,369, 4,664,972, 4,684,712, 4,727,129, 4,727,131, 4,728,714, 4,749,769, 4,762,907, 4,778,927, 4,816,555, 4,849,499, 4,851,496, 4,851,497, 4,857,626, 4,864,013, 4,868,278, 4,882,410, 4,923,947, 4,999,416, 5,015,721, 5,015,722, 5,025,082, 5,086,158, 5,102,935, 5,110,896,

5,143,956, and 5,710,237, each of which is hereby incorporated by reference, and European Patent Application 356,226. A preferred form of LCP is an aromatic polyester or aromatic poly(ester-amide), especially an aromatic polyester. By an "aromatic" polymer is meant that all of the atoms in the main chain are part of an aromatic ring, or are functional groups connecting those rings such as ester, amide, or ether (the latter of which may have been part of a monomer used). The aromatic rings may be substituted with other groups such as alkyl groups. Some particularly preferred aromatic polyester LCPs are those found in U.S. Patent Nos. 5,110,896 and 5,710,237. Another preferred LCP is one containing repeat units derived from terephthalic acid, ethylene glycol, and one or both of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid, or any of their chemical equivalents in polymerization reactions.

Besides other polymers, the LCP (composition) may contain other materials normally found in LCP compositions, such as fillers, reinforcing agents, pigments, lubricants, antioxidants, and filler and reinforcing agents are preferred.

Preferably after one, some or all, more preferably all, of the grinding (in any combination) stages the LCP is classified, at least as to larger or smaller than a certain size. In a two stage grinding process it is also preferred that the LCP is classified after or at the end of the first stage. In grinding processes with more than two stages it is also preferred that the LCP be classified after each stage, except for the final stage. Many types of grinders have interchangeable screens or sieves attached to them and materials is not allowed to exit the grinder until it will pass through the screen attached to the grinder. A screen attached to a grinder is not con-

sidered herein part of the grinder. This is a form of classification. Alternately material exiting the grinder may simply be sieved to size fractions larger or smaller than a certain sieve sizes and/or into size ranges.

5 Useful combinations of grinders to be used in the first and second stage grinding operations are shown below.

First Stage	Second Stage
hammermill	hammermill
disc mill	hammermill
disc mill	disc mill

Other combinations may also be used. In preferred combination the apparatus for the first and second stages is the same, differing only by the size of the screen on the exit port of the grinder, being smaller (higher sieve number) in the second stage, or the clearance between the working (grinding) surfaces is made smaller in the second stage. For example in the first stage one can grind to about 5 to about 30 mesh, preferably about 5 to about 15 mesh, while in the second stage one can grind to about 20 to about 100 mesh, preferably about 30 to about 70 mesh. If a third grinding stage is done, it is preferred that the product be ground to about 60 to about 150 mesh. By grinding to (equal to or smaller than) a certain mesh size in this instance means at least about 90 weight percent, more preferably at least about 99 weight percent, of the LCP can pass through a sieve of the desired size. These sieve size ranges overlap. As noted above the average particle size will be reduced in any grinding stage.

Many grinders have adjustments which may be made to them, such as clearance between the grinding surfaces or elements. If the same (type of) grinder is used in more than one grinding stage, changes can be made to these ad-

justments may be different in different grinding stages. Some of these adjustments often influence the size of the particles which are produced by the grinder, and so the size of the particles produced in that grinding stage are
5 determined, at least part, by these adjustments.

The LCP may be ground dry or wet, that is with or without the presence of a substantial amounts of a liquid, which may also act as a coolant for the grinding process. In addition a liquid such as water may be used
10 as a "carrier" in one or more grinding stages, particularly when it is desired to produce a pulp of the LCP. Such pulps (or water dispersions of LCPs which are ground dry) are particularly useful for forming nonwoven sheets or papers by typical papermaking techniques.

15 In some instance, especially when the LCP is ground dry, it is preferred to cool the LCP, for example with dry ice or liquid nitrogen. This sometimes allows the grinder to more easily break up the LCP particles which are fed to it.

20 In the Examples, except as noted, all of the LCP used had the composition as that of Example 4 of U.S. Patent No. 5,110,896 of hydroquinone/4,4'-biphenol/terephthalic acid/2,6-naphthalenedicarboxylic acid/4-hydroxybenzoic acid in molar ratio
25 50/50/70/30/320.

In the Examples by a "pulp" is meant fibrous material suspended in water.

In the Examples the following apparatus is used:

Sprout-Waldron mills are made by Andritz Sprout-
30 Bauer, Inc., Muncy, PA 17756, USA

Bantam® Mikro pulverizer was made by Division of MikroPul, United States Filter Corp. Summit, NJ 07901, USA

Ahlstrom Master Screen F1 was made by Ahlstrom Machinery Corp., FIN-48601, Kaphula, Finland

Mean length of LCP pulp was determined on the Fiber Quality Analyzer (OpTest Equipment, Inc., 900 Tupper
5 Street, Hawkesbury, Ontario, Canada K6A353)

Example 1

Strand cut pellets of LCP were ground in a 30.5 cm diameter Sprout-Waldron model 12-2C-2976-A single rotating disc refiner equipped with plates in one pass with
10 the gap between plates of about 25 μ m, a feed speed of about 60 g/min. and continuous addition of water in quantity of about 4 kg of water per 1 kg of the pellets. The resulting LCP pulp was additionally ground in a Bantam® Mikro Pulverizer, Model CF, to pass through a 30 mesh
15 screen. The final pulp had arithmetic, length weighted, and weight weighted mean lengths of 0.21, 0.65, and 1.40 mm respectively.

Example 2

The LCP used had the composition of the LCP of Example 9 of U.S. Patent 5,110,896, hydroquinone/4,4'-
20 biphenol/terephthalic acid/2,6-naphthalenedicarboxylic acid/4-hydroxybenzoic acid in molar ratio 50/50/85/15/320. The particulate LCP was prepared by grinding a melt blend of LCP (70 wt. %) and a polytetra-
25 fluoroethylene powder (30 wt. %) in a Bantam® Mikro Pulverizer (model CF) along with liquid nitrogen until the particles passed through about a 10 mesh screen. The particles were reground in the same unit with additional liquid nitrogen until they passed through a 40 mesh
30 screen.

Example 3

Strand cut pellets of LCP were ground on 30.5 cm diameter Sprout-Waldron type double disc refiner model 12-2, equipped with plates type C-2976-A in one pass using an

interdisc gap of 25 μm , feeding speed of about 60 g/min. and continuous addition of water in quantity of about 4 kg of water per 1 kg of the pellets. This LCP pulp was additionally ground (without removing the water from the first step) with about an additional 1 kg water/kg dry product in a Bantam® Mikro Pulverizer, Model CF, to pass through a 60 mesh screen. Final pulp had arithmetic, length weighted, and weight weighted mean lengths of 0.18, 0.39, and 0.86 mm respectively.

10 Example 4

The 40 mesh particulate LCP was prepared by rough grinding an LCP having the composition of Example 9 of U.S. Patent 5,110,896 of hydroquinone/4,4'-biphenol/terephthalic acid/2,6-naphthalenedicarboxylic acid/4-hydroxybenzoic acid in molar ratio 50/50/85/15/320, and which also contained 30% by weight glass fiber, and was in the form of resin pellets (right circular cylinders approximately 1/8" in diameter and length) in a Bantam® Mikro Pulverizer, Model CF, with liquid N₂ also present, and with a coarse (about 10 mesh) discharge screen. The course cut resin was then placed back in the Bantam® Mikro Pulverizer, Model CF, with additional liquid N₂ until the final product passed through a 40 mesh screen.

25 Example 5

Pellets of LCP were ground in a 91.4 cm diameter Sprout-Waldron Model 36-2 single rotating disc refiner with equipped with plates type 16808, with a gap between plates of about 0.73 mm, at feeding speed of about 1.5 kg/min., with addition of about 98.8 kg of water per kg of the pellets. After a first pass, pulp produced was diluted to consistency of about 0.8 wt.% and ground a second time with double recirculation of the slurry through the refiner at gap between discs of about 0.25

mm. Refined LCP pulp was screened through an Ahlstrom F1 Master Screen with slots 0.36 mm wide (about 45 mesh). Final pulp had arithmetic, length weighted, and weight weighted mean lengths of 0.14, 0.45, and 1.82 mm respectively.

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CLAIMS

What is claimed is:

1. A grinding process for forming small particles from larger particles of an anisotropic thermotropic liquid crystalline polymer, comprising:
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(a) a first grinding stage wherein said anisotropic thermotropic liquid crystalline polymer is ground in a first grinding apparatus;

(b) removing said anisotropic thermotropic liquid crystalline polymer from said first grinding apparatus;
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(c) a second grinding stage wherein said anisotropic thermotropic liquid crystalline polymer from (b) is ground in a second grinding apparatus; and

(d) removing said anisotropic thermotropic liquid crystalline polymer from said second grinding apparatus.
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2. The process as recited in claim 1 wherein said thermotropic liquid crystalline polymer contains one or more other ingredients.

3. The process as recited in claim 1 wherein said thermotropic liquid crystalline polymer is a blend with one or more other polymers.
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4. The process as recited in claim 1 wherein said thermotropic liquid crystalline polymer is classified after one or more of said first grinding stage and said second grinding stage.
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5. The process as recited in claim 1 wherein said grinding is done dry.

6. The process as recited in claim 1 wherein said grinding is done wet.

7. The process as recited in claim 1 wherein at least about 90 weight percent of a product of (d) passes through a 30 mesh screen.
30

8. The process as recited in claim 1, wherein at least about 90 weight percent of a product of (d) passes through a 60 mesh screen.

9. The process as recited in claim 1 herein said
5 thermotropic liquid crystalline polymer is an aromatic polyester.

10. The process as recited in claim 1 additionally comprising one or more additional grinding stages.

11. The process of claim 1 wherein said first
10 grinding apparatus and said second grinding apparatus are the same or different.