ROTATIONALLY MOLDED LIQUID CRYSTALLINE POLYMERS

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SUMMARY: Rotational molding is a unique process for producing hollow plastic parts. Rotational molding offers advantages of low cost tooling and can produce very large parts with complicated shapes. Products made by rotational molding include water tanks with capacities up to 20,000 gallons, truck bed liners, playground equipment, air ducts, Nylon fuel tanks, pipes, toys, stretchers, kayaks, pallets, and many others. Thermotropic liquid crystalline polymers are an important class of engineering resins employed in a wide variety of applications. Thermotropic liquid crystalline polymers resins are composed of semi-rigid, nearly linear polymeric chains resulting in an ordered mesomorphic phase between the crystalline solid and the isotropic liquid. Ordering of the rigid rod-like polymers in the melt phase yields microfibrous, self-reinforcing polymer structures with outstanding mechanical and thermal properties. Rotational molding of liquid crystalline polymer resins results in high strength and high temperature hollow structures useful in a variety of applications. Various fillers and reinforcements can potentially be added to improve properties of the hollow structures. This paper focuses on the process and properties of rotationally molded liquid crystalline polymers.

KEYWORDS: Rotational molding, liquid crystalline polymers

INTRODUCTION

Rotational molding is a unique process for producing hollow plastic parts. Rotational molding offers low cost tooling and can produce very large parts with complicated shapes. Products made by rotational molding include water tanks with capacities up to 20,000 gallons, truck bed liners, playground equipment, air ducts, Nylon fuel tanks, pipes, toys, stretchers, kayaks, pallets, corn harvester points, and many others.

Rotational molding forms hollow structural parts adopting the shape of the inside wall of the mold. There are four basic steps in the rotational molding process. (1) The first step involves adding a weighed amount of granulated plastic in one half of a mold. The mold is mounted onto a machine and closed using clamps or bolts. In the second step, the mold is rotated biaxially about a perpendicular axis and put into an oven. The mold is heated to a temperature where the plastic granules can melt and fuse together. As the material melts and becomes tacky, it sticks to the mold wall in successive layers to form the part. After melting and consolidation of the material, the mold is cooled below the melting or solidification point of the plastic material. Rotation continues during cooling to prevent sagging of the material. The final step involves removing the part from the mold.

High performance, light-weight materials are needed in cryogenic storage devices planned for future transportation systems. Rotational molding is a process well suited to make hollow tubing and liners used in cryogenic storage devices. However, materials commonly used in rotational molding such as high density polyethylene, nylon and polycarbonate do not have sufficient physical properties for use in

cryogenic applications. Materials used in cryogenic applications should have low thermal expansion, low gas permeability, high tensile strength, modulus and fatigue resistance. (2) Low temperature properties of thermotropic liquid crystalline materials warrant their consideration in cryogenic applications. (3)

Thermotropic liquid crystalline polymers (TLCP) are an important class of engineering resins employed in a wide variety of applications. TLCP are composed of semirigid, nearly linear polymeric chains resulting in an ordered mesomorphic phase between the crystalline solid and the isotropic liquid. Ordering of the rigid rod-like polymers in the melt phase yields microfibrous, self-reinforcing polymer structures with outstanding mechanical and thermal properties. TLCP can achieve high tensile strength and tensile modulus. TLCP can also maintain these properties in cryogenic environments and up to temperatures approaching 350°C. As structural components, TLCP exhibit low coefficients of thermal expansion and high creep resistance contributing to good dimensional stability. Properties of a typical TLCP are listed in Table 1.

Table 1 – Properties of a neat TLCP material (4)

Property	Typical Value
Water absorption, 24 hr immersion	0.01%
Processing Melt Temperature	340°C
Tensile Stress at Break	145 MPa
Tensile Modulus	10 GPa
Impact Strength, Unnotched (23°C)	950 J/m
Impact Strength, Unnotched (-30°C)	600 J/m
Deflection Temperature @ 1.82 MPa	280°C

Several TLCP are sold commercially into fiber, film and molded parts. These resins are principally aromatic polyesters and polyamides produced by condensation polymerization. Common monomers used in producing TLCP resins are depicted in Figure 1. Each of these resins is offered in a range of grades; including different compositions, melt temperatures, and fillers. For example, Ticona's Vectra A and Vectra B TLCP resins include 2,6-hydroxynaphthoic acid in their formulations. Vectra A is prepared with a 73/27 molar ratio of p-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid, while Vectra B contains a 60/20/20 molar ratio of 2,6-hydroxynapthoic acid, p-hydroxyacetaniline, and terephthalic acid. (5)

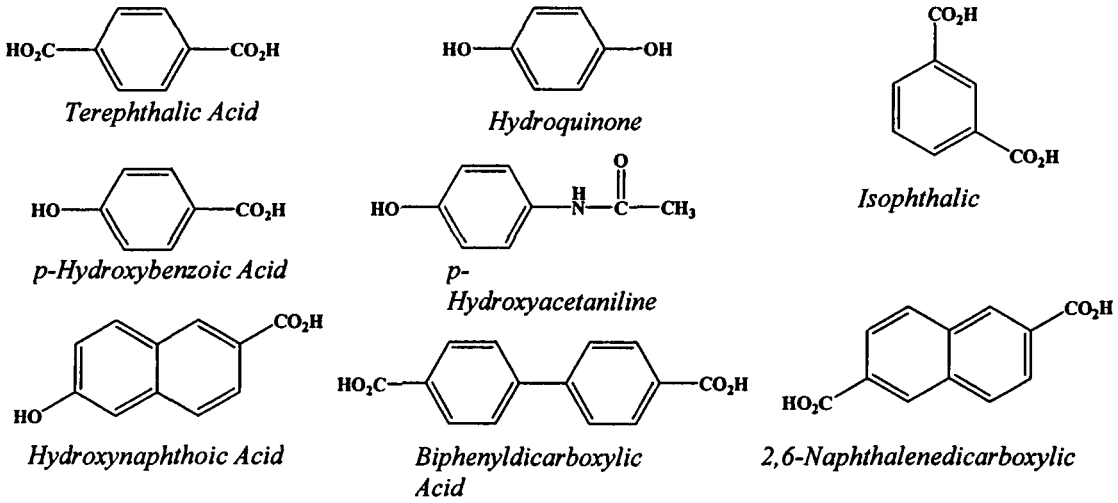

Figure 1. Typical monomers used in TLCP resins

Commercially, thermotropic liquid crystalline polyesters are produced by a melt acidolysis polycondensation reaction. (6) Melt acidolysis involves combining the acetyl derivatives of aromatic hydroxyl compounds and aromatic dicarboxylic acids. The aromatic monomer mixtures are generally heated above the melting point of the monomers to temperatures of 250 to 280°C. The initial stages of melt acidolysis are done under a nitrogen purge. During the second stage of the reaction the temperature is raised to 280 - 360°C to keep the polymer molten. The second stage is done under reduced pressure to remove acetic acid and drive molecular weight growth. The polymerization can proceed without a catalyst or a metal catalyst such as tin or titanium compounds can be added to increase conversion rates. When high conversion is reached the viscous polymer melt is generally extruded and pelletized. If higher molecular weight is desired then solid phase polymerization is conducted. Solid phase polymerization of the ground materials or pellets is conducted within 20 to 30°C below the melting point under vacuum or with a nitrogen purge.

TLCP parts have the following major advantages over other plastic materials used currently used in rotational molding: a) TLCP resins can be used in high heat environment as well as under cryogenic conditions. TLCPs have excellent thermal stability and maintain mechanical integrity at temperatures as high as 350°C. b) TLCP resins have low coefficients of thermal expansion that can be matched to glass, ceramics and metals through resin selection and parts. (7) TLCP materials undergo only minimal dimensional changes from high temperatures to cryogenic environments. c) TLCP resins have exceptional mechanical strength and stiffness allowing parts to bear significant loads without deformation or failure. d) TLCP resins have very low water absorption and high chemical resistance enabling there use in humid or corrosive environments. e) TLCP resins have an inherent resistance to burning and very low smoke generation. f) With densities similar to other thermoplastic materials, TLCP resins enable the production of lightweight materials.

RESULTS AND DISCUSSION

Rangarajan and co-workers originally reported on the use of Vectra B950 in rotational molding and demonstrated that static sintering of Vectra B950 particles produced parts with superior mechanical properties compared to sintered HDPE particles. (8) Comparisons have been made between parts produced by static sintering and parts made by rotational molding of Vectra B950 particles. Vectra B950 particles were statically sintered into tensile bars and tested. All tensile bars were sintered in a 0.5" x 2.5" mold with an exposed top surface and a thermocouple fixed in the center of the side wall. Nitrogen was

supplied through a chamber that covered the mold. The entire unit was then placed in a hot press. The heating soak time was 40 minutes and began once the maximum temperature (320°C) was reached.

Laboratory scale rotational molding was also performed with the Vectra B950 particles. The mold was a stainless steel cylinder (3.81 cm diameter and 7.62 cm long) with both ends capped. One end was fixed to a shaft that was driven by an electric motor rotating at 10 rpm. The other cap had an opening so that a thermocouple could be installed to monitor the air temperature within the mold. Heat was provided by a convection oven equipped with a nitrogen purge and capable of heating rates up to 60°C per minute. The heating cycle was designed to mimic static sintering conditions. The molded product was then sectioned and strips were used for tensile measurements. Surface pitting was observed on all surfaces in contact with the mold but the free (internal) surfaces are smooth and pore free.

The sintered bars and rotationally molded bars were tested with an Instron 4202 using a crosshead speed of 1.27 mm/min and a 30.5 mm gauge length (ASTM standard).Both the tensile strength and modulus of the rotationally molded samples were significantly improved over the statically sintered samples. The rotationally molded samples had a tensile strength of 17.50 MPa and tensile modulus of 2.022 GPa while the static version was 10.51 MPa and 0.930 GPa, respectively. For comparison, Ticona reports the tensile strength of 135 MPa and tensile modulus of 17 GPa for injection molded samples. (9)

Figure 2 depicts the fracture surface of the rotationally molded samples and static sintered samples. Both the samples have significant void contact throughout the thickness. A rough examination of the void area in the fractured surface by image analysis indicates fewer voids in the rotationally molded samples possibly resulting in the better tensile properties. Further efforts to reduce void content during rotational molding should result in further improvements in mechanical properties.

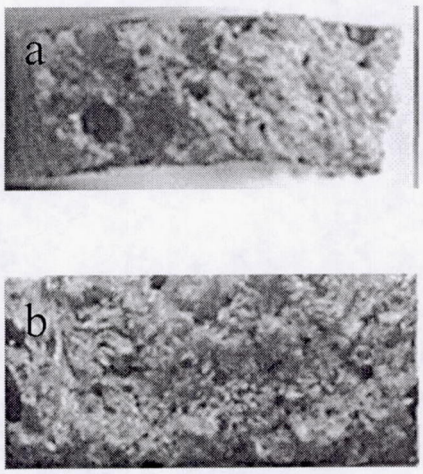

Figure 2 – Fracture surface of a) rotationally molding sample and b) static sintered sample

Figure 3 depicts a rotationally molded tube made from Vectra B950. The laboratory scale molding was performed with a 1.5" diameter x 3" long mold. All trials used resins dried for at least 24 hrs at 100 °C. Cylinders were produced from 40 grams of Vectra B950 granules. The oven temperature was set at 330°C and was controlled to within ±1°. This was to ensure the mold cavity temperatures reached at least 320°C. The rotation was set at approximately 5 rpm. Cycle time was set to 30 minutes once the oven set point was reached. After 30 minutes at the set point the oven was shut off and opened to allow the still rotating mold to cool. The resulting cylinders were continuous with a fairly uniform wall thickness. Some bubbles were trapped against the mold surface during densification.

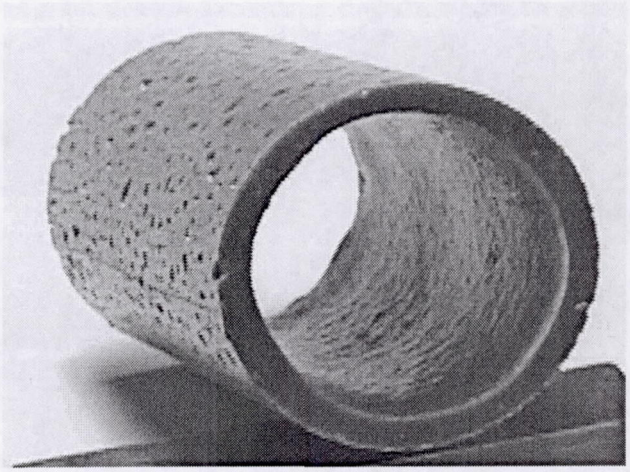

Figure 3 - Laboratory scale rotationally molded tubes 1.5" x 3"

A burst test device was conceived and designed as shown in Figure 4. The device is designed to fit the 1.5 inch diameter tubes. The design consists of two aluminum plates, with recesses cut out for the test sample, holes drilled at the corners for reinforcing bars, and a normal pipe thread (NPT) type fitting in the center of one plate for delivering pressurized fluid. The sample tube (brown) is shown enclosed in the fixture. The fluidic seals were made with rubber gasket material, and the ends were sealed with silicone grease.

One of the rotationally molded tubes from was attached to a burst test apparatus. The tube had an average thickness of 2.12 mm. The tube was pressurized to 68 psig in helium without signs of leakage (as determined by submerging the pressurized part under water) and was subsequently pressurized with silicone oil to 230 psig before bursting.

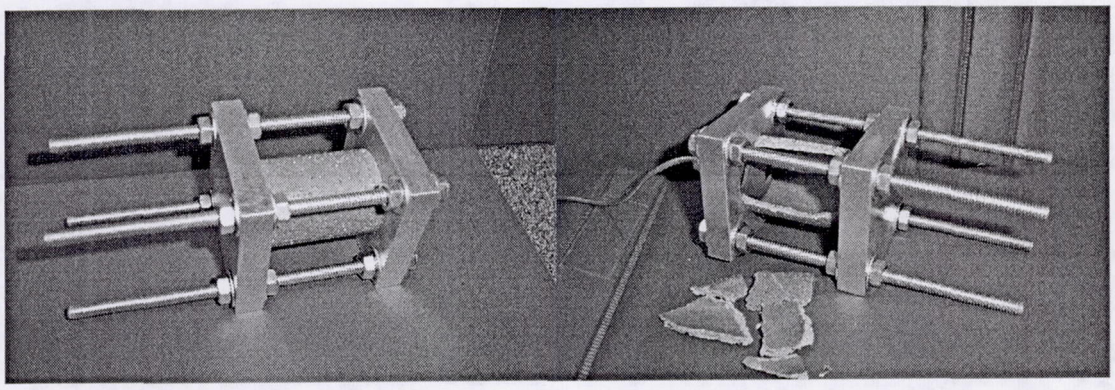

Figure 4 - LCP tube in pressure test device, before and after test

The ability to produce TLCP hollow structures by rotational molding has been demonstrated. Future efforts will focus on optimizing the various processes involved in producing TLCP rotationally molded parts and demonstrating use in cryogenic applications.

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