

Thermotropic liquid crystalline polymers as protective coatings for aerospace

Gustavo Guerriero*, René Alderliesten, Theo Dingemans, Rinze Benedictus

Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands

ARTICLE INFO

Article history:

Received 2 June 2010

Received in revised form 29 August 2010

Accepted 1 September 2010

Keywords:

Liquid crystalline polymer

Coating

Thermoset

Adhesion

Mechanical properties

Chemical resistance

ABSTRACT

Liquid crystalline polymers (LCPs) have potential as multifunctional, environmentally friendly coatings for aerospace, overcoming the disadvantages of current materials. Their use, however, has been hindered mainly by their poor adhesion strength. The present work studies novel liquid crystalline thermosetting polymers (LCTs), which can overcome the disadvantages of commercial LCPs for protective coatings in aerospace applications. Phenylethynyl terminated liquid crystalline oligomers based on 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) were synthesized and melt-pressed on grit-blasted aluminum to obtain 25 μm and 80 μm thick coatings. The presence of coating defects and curing kinetics were investigated, and the adhesion, mechanical properties and environmental resistance were compared with a commercial LCP reference material (Vectra®). The LCTs showed highly improved adhesion; moreover, fully cured LCTs are harder and stiffer than commercial LCPs, which are expected to increase their wear and impact resistance. The coatings showed no swelling, peeling, or blistering after 500 h of full immersion in fluids such as jet fuel and turbine oil; furthermore, LCTs resisted 1000 h in corrosive fog (salt-spray) and hot moisture. Exposed samples retained their hardness, modulus, and pull-off strength, evidencing the outstanding chemical resistance of these LCTs. Our findings showed the potential of LCTs as protective and wear resistant coatings, particularly in the aggressive environments of aerospace applications. However, results suggest that exposed coating/substrate interfaces constitute paths for environmental attack. Further research aims at elucidating the possible mechanisms.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The importance of liquid crystalline polymers (LCPs) for coating applications has been recognized by academic and industrial researchers, due to their outstanding combination of fracture toughness, chemical resistance, and barrier properties over a wide temperature range [1–3]. These properties are mainly obtained due to the formation of an ordered melt, or liquid crystalline phase (mesophase), which produces a self-reinforcing phenomenon [4]. Thermotropic refers to LCPs (TLCPs) where the mesophase is formed in the melt. TLCPs are usually less affected by the environment than lyotropic LCPs, in which the mesophase is obtained in solution. One of the most studied TLCPs is the thermoplastic Vectra® (Ticona GmbH), which exhibits an exceptionally low coefficient of thermal expansion (CTE), high temperature stability and chemical resistance [5]. Vectra is especially suitable for injection molding and has been used in many electronic and medical applications. It has been very attractive for applications such as food packaging, despite their higher cost per unit weight, since equal barrier properties can be obtained with much thinner films, which results in reduced total costs [6].

Complex manufacturing processes and poor adhesion properties have restricted the use of TLCPs in coating applications and coextruded films. The inert surfaces of TLCPs, of main importance for their chemical resistance, provide neither the physical nor chemical bonds required for good adhesion with other surfaces [7]. Several authors have investigated diverse surface treatments to enhance adhesion in applications like packaging or printed circuit boards, but with limited results (see, for example, [8–10]). In addition, they have high melt processing temperatures and a hierarchical fracture behavior, which makes it inherently difficult to grind TLCPs and obtain powder suitable for powder-coating techniques. As a consequence, despite the impressive literature on TLCPs, a very limited number of studies have approached TLCPs as resins for coating applications [2,11,12]; and these studies focused mainly on manufacturing and documentation of a few basic properties.

Recently, a new family of phenylethynyl end-capped Vectra-based oligomers was introduced. The phenylethynyl groups have been previously used to develop thermosetting resins for aerospace structural applications [13,14]. These new end-capped TLCPs can be melt-processed within a wide temperature window, in which the reactive end-groups remain latent. Further heating above the cure onset temperature activates the end-groups, and via chain extension and crosslinking, a fixed three-dimensional network is obtained [15]. It has been shown that the end-group chemistry

* Corresponding author. Tel.: +31 015 278 9282; fax: +31 015 278 1151.

E-mail address: G.L.Guerriero@tudelft.nl (G. Guerriero).

does not interfere with the formation of the liquid crystalline phase [15,16]. At the same time, these LCTs are expected to have increased surface activity due to the end-group polarity. Therefore, these new LCTs are predicted to have the aforementioned properties inherent to TLCPs, with greatly improved adhesion properties. Another advantage of these LCTs is that due to the lower mechanical properties of the reactive oligomer intermediate, they can be easily milled into fine powders suitable for powder-coating applications. One may then expect these new LCTs to overcome the drawbacks of commercial TLCPs and be successful protective coatings, especially in aggressive environments such as hydraulic fluids or de-icing agents used in aerospace applications.

The aim of the present work is to demonstrate the potential of these new phenylethynyl terminated TLCPs for coating applications. The thermal properties and curing of the LCT were investigated, and the resulting coating quality was assessed. Surface morphology and mechanical properties were evaluated, followed by lap-shear and pull-off strength measurements. The resistance to corrosive environments and hot moisture were tested, and the resistance to different fluids present in the aerospace industry, like kerosene based fuels, hydraulic fluids (such as Skydrol®), de-icing liquids and specialized cleaning agents, was evaluated by immersion tests. Finally, the environmental effects on the adhesion and mechanical properties were assessed in an attempt to investigate the durability of the coating.

2. Materials and methods

2.1. Materials

To synthesize the phenylethynyl terminated liquid crystalline thermosets, all chemicals were obtained from the indicated sources and used as received. For the end group synthesis, 4-phenylethynylphthalic anhydride (4-PEPA) was purchased from Daychem Laboratories Inc. (Ohio, USA) and 4-aminobenzoic acid was obtained from Acros Organics B.V.B.A. (Geel, Belgium). Acetic acid and 4-aminophenol were purchased from Sigma-Aldrich Inc. (Missouri, USA). For the oligomer syntheses, we obtained 4-hydroxybenzoic acid (HBA) and potassium acetate from Acros Organics B.V.B.A., and acetic anhydride from Sigma-Aldrich Co.; 6-hydroxy-2-naphthoic acid (HNA) was provided by Ueno Chemicals Ltd. (Hyogo, Japan). The 5000 g mol^{-1} reactive oligomer was synthesized according to a procedure previously reported by Knijnenberg et al. [15]. All thermal treatments and curing cycles were performed under vacuum.

The non-end-capped HBA/HNA liquid crystalline polymer used, Vectra A950, is a commercial LCP manufactured by Ticona GmbH (Kelsterbach, Germany). Substrates consisted of a 2 mm thick aluminum AA5083-H111 (Salomon's Metalen B.V., Groningen, The Netherlands), a non-heat treatable aluminum alloy.

2.2. Coating preparation

Aluminum substrates of 150 mm by 100 mm were thoroughly cleaned with an industrial solvent (PFSR, PT Technologies, Watergrasshill, Ireland) and ethanol. The substrates were grit-blasted with 90–150 μm glass beads right before the coating application, to ensure a freshly exposed aluminum surface. All panels were grit-blasted on both sides to reduce deformation due to induced residual stresses. After grit-blasting, the panels were cleaned with an air jet to remove residual metallic particles and glass beads.

All coatings were prepared in a similar fashion. The polymers were melt-pressed on to the aluminum substrate using a computer controlled hot-press LAP100 (Gottfried Joos Machinefabrik GmbH & Co. KG, Pfalzgrafenweiler, Germany). Kapton® films, 25 μm and

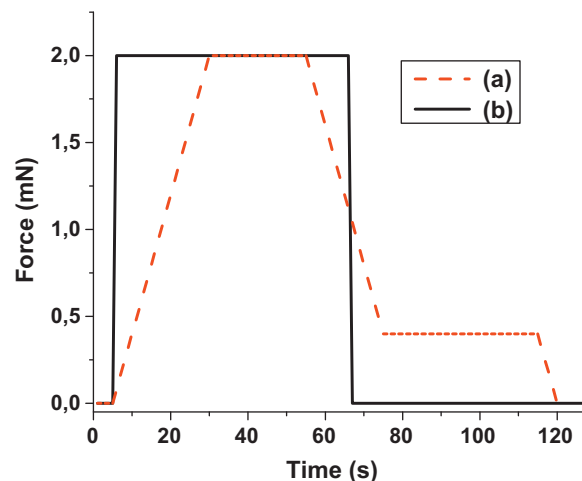


Fig. 1. Traditional (a) and step (b) loading profiles used for the nanoindentation of the LCP coatings.

80 μm thick, were used to control the thickness of the coatings and as a release film for the mold. The mold was heated to 310 °C at a rate of approximately 8 °C/min without applied force. Once the system reached the indicated temperature, a pressure of 2.5 MPa was applied. The system was held at 310 °C and 2.5 MPa for 4–5 min; the temperature was then reduced to 30 °C at 10 °C/min. The LCTs were cured for 1 h under vacuum at two temperatures: 350 °C and 370 °C. For simplicity, this paper will refer to the coatings cured at 350 °C as LCT-A, and as LCT-B to the coatings cured at 370 °C. The heating and cooling rates of the vacuum oven were approximately 6 °C/min and 0.5 °C/min, respectively.

2.3. Characterization methods

Thermal analyses were performed using a differential scanning calorimeter (DSC, Sapphire) and a thermo balance (TG/DTA, Pyris Diamond), both from PerkinElmer, Inc. (Massachusetts, USA).

Surface morphology was investigated using lower secondary electron imaging in a field emission scanning electron microscope (SEM, JSM-7500F, Jeol Ltd., Tokyo, Japan), with a Gallium source accelerated at 5 kV, and a confocal laser scanning microscope LEXT OLS 3100 (Olympus GmbH, Hamburg, Germany) was used for roughness measurements. For SEM analysis, samples were prepared by sputtering an ultrathin gold layer to avoid electrostatic charging on the surfaces. Coating cross-sections were polished to a 1 μm finish and examined by optical microscopy (Leyca A100). No etching was required.

2.3.1. Nanomechanical properties

Nanoindentation was performed with a scanning probe microscope (SPM, Hysitron, Minneapolis, USA), using a standard Berkovich indenter. Since significant creep-like behavior and time/rate-dependent results are expected during nanoindentation of visco-elasto-plastic materials [17], such as LCPs, two load controlled modes with a maximum load of 2 mN were selected based on Dub and Trunov [18]. The first was a traditional one, widely used in nanoindentation (Fig. 1), while the second method is a step-loading with rapid (1 s) loading and unloading segments, and 60 s hold segments at the peak load and after unloading. Typically, 9 indents were obtained for individual specimens; Oliver and Pharr's method [19] was used to analyze the unloading section of the nanoindentation load–displacement curves of the LCPs, and average values were calculated.

Download English Version:

<https://daneshyari.com/en/article/693055>

Download Persian Version:

<https://daneshyari.com/article/693055>

[Daneshyari.com](https://daneshyari.com)