Toughening polymer surfaces

Haider K. Ali

University of Wollongong

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Recommended Citation

Toughening Polymer Surfaces

A thesis submitted in fulfilment of the requirements for the award of the degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

by

Haider K. Ali
MEngSt. (Auckland University)

School of Mechanical, Materials and Mechatronics Engineering
July 2006
DECLARATION

I, Haider K. Ali, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualification at any other academic institution.

Haider K. Ali

July 2006
ACKNOWLEDGMENTS

I would like to express my sincere thanks to my supervisor, Professor Hugh Brown for providing help and support during the course of my study. A grateful acknowledgment is also extended to SOLA Optics for sponsoring this project, and in particular to Dr. David Lewis for his technical input. In addition, I would like to thank the following people for their assistance and support over this work:

Prof. Michael West and his PhD students Bradley Glass and Bane Lake for their support with the FEMCAD software,

Dr. Peter Innis and Mr Avirs Dipers from the School of Science for their instruction regarding the use of Raman spectroscopy and the polariscope located in their department,

Ms Lorelle Pollard for her kindly administration support,

Dr. Chris Lukey, Dr. Wang Huillang, and Ms. Siu Wah Wai from the Polymer Group for their scientific involvement and advice,

Mr. Chandana Herath from the Electrical engineering for his PC support,

Mr. Ron Marshall with his staff at the UOW engineering workshop,

Mr. Greg Tilman and Mr. Bob Dejong for their technical contribution and support.

Also I would like to thank the librarian staff at the UOW general library for their genuine help and assistance.
ABSTRACT

The thermoset resin poly diglycol carbonate, commercially called CR-39 has excellent optical properties, is cheaper than other ophthalmic materials and is considered one of the best plastic materials for the industry. CR 39 is known to be a brittle, highly cross-linked polymer. Applying coating layers significantly affects the toughness of ophthalmic lenses; a crack will first start on the surface of the coating and propagate through to the lens. One procedure to stop cracking, although not favoured by the industry because of its cost and detrimental effect on the optical properties, is to place a thin, rubbery layer between the coating and CR-39 ophthalmic lens.

An alternative method to stop the cracking is to toughen the lens material itself by placing the upper and lower surfaces under compressive stress. Swelling the lens surface can generate compressive stress and generating a multi-composite stressed layer lens can significantly improve fracture toughness.

An axisymmetric model of the spherical lens was built and a static load was applied on the central region in order to analyse stress distribution on the surfaces of the lens. It was found that tensile stress dominates the lower surface when the load was applied on the top surface. A volumetric swelling was introduced into the axisymmetric model to generate compressive stress onto the swollen surface while the tensile stress region on the lower surface was moved towards the central region.
of the spherical lens. The volumetric swelling transferred the stress in the horizontal axis from the tension to the compression region.

More than one system has been designed to evaluate the best swelling agent; chloroform was the best solvent and a mixture of chloroform with acrylic acid (monomer) was found to be the best swelling agent for the CR-39 ophthalmic lens. Ultra Violet (UV) light initiated polymerisation was used to polymerise the monomer within the surface of CR-39 ophthalmic lens. The temperature during this process remained below the glass transition temperature (Tg) of CR-39 polymer.

Raman spectroscopy was used to examine the residual vinyl group in CR-39 polymer and monitor the diffusion process of the monomer in the CR-39 lens surface and the polymerisation process of the diffused monomer. The depth of this treatment was measured by using the mapping technique in Raman spectroscopy. The stress generated from swelling the lens surface was measured by photoelasticity. A 3-point bending device was developed and attached to a circular polariscope to measure the optical stress coefficient of CR-39 because it is a transparent material.

Fracture energy was evaluated using the static impact and dynamic tests and significant improvements from treating both upper and lower surfaces and applying a hard coating to the treated lenses were observed. Surface characterisation techniques were used to determine the effect of the treatment applied to the CR-39 ophthalmic lenses. Ultra-Micro Indentation System (UMIS) analysis measurements using Berkovich and spherical indenters showed a decrease in the elastic modulus. Dynamic Mechanical Analysis (DMA) measurements using the penetration and
Abstract

single cantilever modes showed an increase in loss modulus and a decrease in storage modulus accompanied by a lower compression modulus for the treated surfaces. Atomic force microscopy (AFM) studies revealed that the treated surface of a CR-39 ophthalmic lens was smoother than an untreated surface.
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<thead>
<tr>
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<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AA</td>
<td>acrylic acid</td>
</tr>
<tr>
<td>BEE</td>
<td>benzoin ethyl ether</td>
</tr>
<tr>
<td>BP</td>
<td>benzophenone</td>
</tr>
<tr>
<td>ADC, CR-39</td>
<td>diethylene glycol bis allyl carbonate</td>
</tr>
<tr>
<td>DVB</td>
<td>divinyl benzene</td>
</tr>
<tr>
<td>IPP</td>
<td>diisopropyl peroxydicarbonate</td>
</tr>
<tr>
<td>MAA</td>
<td>methacrylic acid</td>
</tr>
<tr>
<td>ST</td>
<td>styrene</td>
</tr>
<tr>
<td>TBPP</td>
<td>tert-butyl peroxybenzoate</td>
</tr>
<tr>
<td>TBP</td>
<td>tetra-butyl peroxide</td>
</tr>
<tr>
<td>VA</td>
<td>vinyl acetate</td>
</tr>
<tr>
<td>SR, HR</td>
<td>scratch resistance coatings</td>
</tr>
<tr>
<td>AR</td>
<td>anti reflective coatings</td>
</tr>
<tr>
<td>OPS</td>
<td>oxide polishing solution</td>
</tr>
<tr>
<td>UMIS</td>
<td>ultra-microindentation system</td>
</tr>
<tr>
<td>UV</td>
<td>ultra-violet</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
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<td>DMA</td>
<td>dynamic mechanical analysis</td>
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<tr>
<td>USA</td>
<td>United States of America</td>
</tr>
</tbody>
</table>

\[\sigma_x\] stress in x-direction
\[\sigma_{st}\] tensile stress in x-direction
\[\sigma_{sc}\] compressive stress in x-direction
\[P\] pressure load
\[P'\] distributed pressure
\[a\] distance of the applied pressure to the centre of the spherical deformable body
\[r\] radius of the deformable body
\[\rho_g\] grain density ratio
\[\rho'_g\] 
\[k_g\] bulk modulus
\[\theta\] expansion temperature
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_{u_w}$</td>
<td>saturation and the pressure stress in the wetting fluid</td>
</tr>
<tr>
<td>$\varepsilon^v_g$</td>
<td>volumetric thermal strain</td>
</tr>
<tr>
<td>$\alpha_s(\theta)$</td>
<td>thermal expansion coefficient for the solid matter</td>
</tr>
<tr>
<td>$I_L$</td>
<td>laser intensity</td>
</tr>
<tr>
<td>$\nu_o$</td>
<td>wave number of monochromatic beam radiation (from the laser light)</td>
</tr>
<tr>
<td>$\nu_i$</td>
<td>wave number of $i$th vibrational mode</td>
</tr>
<tr>
<td>$d\alpha$</td>
<td>change in polarizability</td>
</tr>
<tr>
<td>$dQ$</td>
<td>change in the normal coordinate length of the vibration</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>$wt_s$</td>
<td>swollen weight</td>
</tr>
<tr>
<td>$wt_{int}$</td>
<td>initial weight</td>
</tr>
<tr>
<td>$C_g$</td>
<td>stress-optical coefficient</td>
</tr>
<tr>
<td>$\Delta n$</td>
<td>change in birefringence</td>
</tr>
<tr>
<td>$R$</td>
<td>relative retardation</td>
</tr>
<tr>
<td>$(P-Q)$</td>
<td>principle stresses</td>
</tr>
<tr>
<td>Stdve</td>
<td>standard deviation</td>
</tr>
<tr>
<td>Br</td>
<td>Brewster</td>
</tr>
<tr>
<td>$E$</td>
<td>elastic modulus</td>
</tr>
<tr>
<td>$t$</td>
<td>thickness</td>
</tr>
<tr>
<td>$E'$</td>
<td>composite modulus</td>
</tr>
<tr>
<td>$D_i$</td>
<td>diameter of the indenter</td>
</tr>
<tr>
<td>$D_{im}$</td>
<td>diameter of the residual impression</td>
</tr>
<tr>
<td>$F$</td>
<td>applied force</td>
</tr>
<tr>
<td>$A$</td>
<td>contact area</td>
</tr>
<tr>
<td>$K_{ic}$</td>
<td>critical stress intensity factor or fracture toughness</td>
</tr>
<tr>
<td>$G_c$</td>
<td>critical strain energy release rate or fracture energy</td>
</tr>
<tr>
<td>$C$</td>
<td>crack length</td>
</tr>
<tr>
<td>$E/H$</td>
<td>modulus to hardness ratio</td>
</tr>
<tr>
<td>$\delta_e$</td>
<td>elastic displacement</td>
</tr>
<tr>
<td>$\nu_m$</td>
<td>Poisson’s ratio for the indented material</td>
</tr>
<tr>
<td>$\nu_i$</td>
<td>Poisson’s ratio for the indenter</td>
</tr>
<tr>
<td>$E_m$</td>
<td>elastic modulus for the indented material</td>
</tr>
<tr>
<td>$E_i$</td>
<td>elastic modulus for the indenter</td>
</tr>
<tr>
<td>$h_{p_{max}}$</td>
<td>plastic penetration at maximum load</td>
</tr>
</tbody>
</table>
List of Principal Symbols

\[ \frac{dP}{dh} \bigg|_{F_{\text{max}}} \quad \text{unloading slope at maximum load} \]

\( F_{\text{max}} \quad \text{maximum indentation load} \)

\( H_b \quad \text{hardness using Berkovich indenter} \)

\( H_{\text{sph}} \quad \text{hardness using the spherical indenter} \)

\( E', E_{\text{storage}} \quad \text{storage modulus} \)

\( E'', E_{\text{Loss}} \quad \text{loss modulus} \)

\( E_{\text{comp}} \quad \text{compression elastic modulus} \)

\( E_{\text{Sph}} \quad \text{elastic modulus measured by UMIS spherical indenter} \)

\( RMS \quad \text{roughness mean squared} \)