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Toughening polymer surfaces

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Toughening Polymer Surfaces

A thesis submitted in fulfilment of the requirements
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from

UNIVERSITY OF WOLLONGONG

by

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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

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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 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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List of Principal Symbols

AA	acrylic acid
BEE	benzoin ethyl ether
BP	benzophenone
ADC, CR-39	diethylene glycol bis allyl carbonate
DVB	divinyl benzene
IPP	diisopropyl peroxydicarbonate
MAA	methacrylic acid
ST	styrene
TBPB	tert-butyl peroxybenzoate
TBP	tetra-butyl peroxide
VA	vinyl acetate
SR, HR	scratch resistance coatings
AR	anti reflective coatings
OPS	oxide polishing solution

UMIS	ultra-microindentation system
UV	ultra-violet
AFM	atomic force microscope
DMA	dynamic mechanical analysis
FTIR	fourier transform infrared spectroscopy
CSIRO	Commonwealth Scientific and Industrial Research Organization
SOLA	Scientific Optical Laboratories of Australia
USA	United States of America

σ_x	stress in x-direction
σ_{xt}	tensile stress in x-direction
σ_{xc}	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
$\frac{\rho_g}{\rho_g^o}$	grain density ratio
k_g	bulk modulus
θ	expansion temperature

su_w	saturation and the pressure stress in the wetting fluid
ε_g^{th}	volumetric thermal strain
$\alpha_g(\theta)$	thermal expansion coefficient for the solid matter

I_L	laser intensity
ν_o	wave number of monochromatic beam radiation (from the laser light)
ν_i	wave number of *i*th vibrational mode
$d\alpha$	change in polarizability
dQ	change in the normal coordinate length of the vibration
Tg	glass transition temperature
wt_s	swollen weight
$wt_{\text{int.}}$	initial weight

C_g	stress-optical coefficient
Δn	change in birefringence
R	relative retardation
$(P-Q)$	principle stresses
Stdve	standard deviation
Br	Brewster

E	elastic modulus
t	thickness
E^*	composite modulus
D_i	diameter of the indenter
D_m	diameter of the residual impression
F	applied force
A	contact area
K_{Ic}	critical stress intensity factor or fracture toughness
G_c	critical strain energy release rate or fracture energy
C	crack length
E/H	modulus to hardness ratio
δ_e	elastic displacement
ν_m	Poisson's ratio for the indented material
ν_i	Poisson's ratio for the indenter
E_m	elastic modulus for the indented material
E_i	elastic modulus for the indenter
$h_{p\max}$	plastic penetration at maximum load

$\left[\frac{dP}{dh}\right]_{F\max}$	unloading slop at maximum load
$F_{\max}$	maximum indentation load
H_b	hardness using Berkovich indenter
H_{sph}	hardness using the spherical indenter
E', $E_{storage}$	storage modulus
E'', E_{Loss}	loss modulus
E_{comp}	compression elastic modulus
E_{Sph}	elastic modulus measured by UMIS spherical indenter
RMS	roughness mean squared