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Enhanced abrasion resistance of ultrathin reflective coatings on polymeric substrates: An improvement upon glass substrates

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ABSTRACT

Multilayer thin film systems on polymeric substrates are investigated as abrasion resistant reflective coatings for the development of light weight optical devices. In this investigation, the influence of the coating's material properties on its abrasion resistance is determined with a step increase in abrasion resistance demonstrated upon application of an ultrathin capping layer, ca. 5–15 nm. These ultrathin capping layers reduce the surface roughness and coefficient of friction of the coating system, resulting in a greater resistance to wear. Despite the soft nature of the underlying polymeric substrate, the engineered coating system allows such devices to outperform their conventional glass-based counterparts in the design of light weight products for a range of optical applications.

1. Introduction

Thin film reflective coatings are used in many optical applications, such as in lasers [1], in smart solar collectors [2], for UV lithography [3] and as decorative coatings [4]. The vast majority of these coatings are deposited onto glass substrates because they adhere well [5], and glass typically possesses desirable mechanical properties (hardness and elastic modulus). Counter to this, glass substrates are relatively heavy in weight, inflexible, and there is a limited range of possible substrate shapes. In an attempt to address the limitations of glass, polymeric materials are being explored as replacement substrates, due to their simple formability and lighter weight [6]. The use of polymeric substrates provide benefit to many real world applications as the reduced weight of the device leads to reduced energy consumption (*i.e.* reduced fuel consumption for vehicles employing polymeric automotive mirrors and windows), combined with differing substrate mechanical properties to create flexible, shatter proof products or low cost architectural materials [7].

A limitation of the polymeric substrates, however is that they are typically much softer than glass, thus implying a comparatively lower resistance to abrasion [8]. To overcome this, a hard coating or coating system (several thin films combined in a layered structure) can be deposited on the polymeric substrate. Many of the hard coatings or coating systems require high substrate temperatures during the deposition process and/or use a high temperature annealing process post-deposition in order to increase the hardness of the coating system [9]. However, polymeric substrates have relatively low glass transition temperatures (*i.e.* 150 °C for most of the polycarbonates [10]) compared to glass (700 °C for soda-lime glass [10]), which limits the temperature of the deposition by which any coating is applied.

Despite the restricted range of temperatures during deposition of a given coating or coating system, optical devices based upon polymeric substrates have been used for many years in the ophthalmic industry, with functional coating systems (anti-reflection [11] or photochromic coatings [12]) being developed for polymeric substrates (such as allyl diglycol carbonate – CR39, PMMA and polycarbonate) [13,14]. In the majority of applications, a thick hard coating (several micrometres thick) of a silicone-based resin is deposited by dip-, spin- or spray-coating [15,16]. This silicone based resin coating is a hard transparent glass-like coating which imparts a high level of abrasion resistance to the polymeric substrate. The resin coatings can also be modified to provide greater functionality, such as matching its refractive index to that of the polymeric material [17], and/or adding UV resistance or anti-reflection [18,19].

The concept of coating polymeric substrates with reflective layers is not new [20], with many consumer products of this kind being introduced to market [21]. However, the majority of these products either do not require a high quality optical finish (*i.e.* food packaging, toys) or are not directly exposed to climatic conditions or abrasive media (*i.e.* automotive head and tail light reflectors) [22]. In recent times there have been several attempts to introduce reflective coating

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systems on polymeric substrates in more “exposed” environments, such as external automotive mirror devices supplied by VTEC, Venture- source, Ficocipa, Specchidea and Sabic. The major proportion of these products have had limited success in the market place due to the poor resistance to abrasion (of the combined polymeric substrate plus coating system) [23].

When the optical coatings are employed in automotive mirror applications there is a requirement for the coating system to be of high enough reflectivity (*i.e.* greater than 35% in the case of the legal requirements for automotive mirrors in Canada [24]) and of neutral colour (CIELAB a^* and b^* values for reflected light should be as close to 0 as possible [25]). Among the different materials employed to achieve this, the most common in use are silver, aluminium and chromium [26]. Although silver and aluminium have the highest reflectivity (98% and 90% respectively [10]), they are softer than chromium. The use of chromium therefore gives the advantage of being both hard and sufficiently reflective. In practice, the hardness of the reflective chrome coatings can be further enhanced by doping to form nitrides, borides or carbides [27]. This however has a detrimental effect on the optical properties by altering its colour and reflectivity, thus reducing its range of application. The alternative, novel approach to circumvent this involves doping chromium with other transition metals in order to form a nano-composite material [28]. Such coating systems provide a hard reflective film which is neutral in colour.

With respect to the wear of these reflective, or in fact any, coating system, the degradation can be observed as either delamination, scratching or pitting [29]. Means by which to overcome this degradation include increasing the hardness of the coating system, reducing the overall surface roughness of the coating, and by the reduction of the coefficient of friction [30]. The focus of this study is to investigate these effects through modification of the reflective coating system. More specifically, ultrathin capping layers (ca. 5–15 nm) are introduced to modify the above mentioned properties in order to produce wear resistant reflective coating systems on polymeric substrates. The specific ultrathin capping layers are chosen so as not to substantially change the colour of the coating system. These devices then serve as replacement products for their commercially available counterparts which are based upon glass substrates.

2. Experimental details

2.1. Sample deposition

Transparent polycarbonate substrates (cut to approximately 8 cm × 8 cm squares of 0.5 cm thickness) were spin-coated with CrystalCoat^{TM} PR-660 primer plus MP-101 transparent hard coat resin system (SDC Technologies) to form pre-coated substrates. For the chosen hard coat system the primer was applied to a thickness of 0.5 μm and the hard coat resins was applied to a thickness of 5 μm and then thermally cured according to the manufacturer's prescribed specifications (ca 125 °C for 1 h).

Hard coated substrates were placed into a custom built magnetron sputtering reaction chamber, pumped down to 1×10^{-4} mbar with the pre-coated substrate heated to a temperature of 85 °C using an infrared lamp, and then coated with a 135 nm SiO_2 layer and a 60 nm $CrZr_{0.03}$ alloy layer. The thickness of the hard coat resins and SiO_2 coating were measured using a F20 Thin Film Analyser by Filmetrics Inc., while the thickness of $CrZr_{0.03}$ alloy coating was measured using a NT-MDT NTEGRA Prima AFM. The SiO_2 coating was sputtered from a high purity Si target in an $Ar+O_2$ environment on a rotating sample holder at a working pressure of 3.2×10^{-3} mbar over a 9 min deposition time. The $CrZr_{0.03}$ alloy coating was deposited (without delay or venting) in the same chamber by simultaneous co-deposition for 1.7 min from a Cr and a Zr target with the applied power to the targets balanced to achieve 2.8 at% Zr concentration in the alloy determined by X-ray Photoelectron Spectroscopy (XPS, Specs) (previously found to be the hardest among Zr doped Cr alloys [31]).

Table 1
The list of the examined coating systems.

Sample reference	Base coatings	Capping layer
PR660/ MP101	PR660/ MP101/ SiO_2/ $CrZr_{0.03}$	N/A
Hydrophilic	PR660/ MP101/ SiO_2/ $CrZr_{0.03}$	5 nm SiO_2
Hydrophobic	PR660/ MP101/ SiO_2/ $CrZr_{0.03}$	5 nm SiO_2/ 10 nm SH-HT VACO
Protective	PR660/ MP101/ SiO_2/ $CrZr_{0.03}$	5 nm SiO_2/ Siloxane

A range of different ultrathin capping layers were then deposited onto the $CrZr_{0.03}$ alloy for comparison with the uncapped samples. The coating systems for each of the respective samples are listed in Table 1.

To maximise the stability of both the hydrophobic and the protective capping layers a 5 nm SiO_2 layer was deposited as an adhesion layer (a typical approach for many applications [14]). In light of this, an additional control sample was created which consisted of just the SiO_2 layer by itself; this layer alone is a well known hydrophilic and anti-fogging coating [32]. This SiO_2 capping layer was deposited onto the $CrZr_{0.03}$ coating in the same sputtering system, using the same deposition conditions as described above but using a 20 s deposition time. With respect to the hydrophobic coating, the SiO_2 adhesion layer with a 10 nm hydrophobic capping layer was applied in an e-beam evaporation system pumped down to 7×10^{-5} mbar using high purity SiO_2 granules and SH-HT VACO (DON CO., LTD.) tablets. The final capping layer (herein referred to as a Protective coating) comprised of a plasma polymer film which is commonly used as a protective coating against corrosion [33] and is derived from hexamethyldisiloxane (HMDSO) monomer. This Siloxane coating was deposited at a pressure of 3.6×10^{-2} mbar using an electrode power of 5 kW at a frequency of 40 kHz onto the SiO_2 layer in a commercial vacuum deposition system (Leybold Optics).

2.2. Sample characterisation and testing

The optical parameters of the coating systems, Reflectance-specular included (RSI), Reflectance-specular excluded (RSE) and Transmission (T%), were measured using a HunterLab UltraScan Pro instrument with 8° measurement angle, CIE Standard Illuminant A and CIE1931 2° Standard Observer. The reflected haze (H) was calculated from $H(\%)=(\text{RSE}/\text{RSI})\times100$ as per SAE J964, and used as a measure of the magnitude of abrasion resistance for the coating systems.

The macroscopic abrasion resistance of the coating systems were tested using an Oscillating Abrasion Tester (model 6100) from Taber Industries, as per the previously reported procedure [34] with an additional front surface coated glass mirror (Flabeg Deutschland GmbH) used as a reference sample. In this study the performance of the samples were assessed at 100 cycle increments up to 800 cycles to investigate the coating systems variation in abrasion resistance. The abrasion resistances of the coating systems were compared with respect to their change in H and change in ΔT% as a function of the number of abrasion cycles.

The friction and topography of the coating systems were characterised using lateral force microscopy (NT-MDT NTEGRA Prima SPM) using a NT-MDT contact mode CSG10 tip with a normal spring constant of 0.138 N/m (Sader technique [36]). At the given set-point of the instrument, the force applied to the surface of the coating system was approximately 36 nN, as