Investigations into mechanical durability of thin display coatings

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Abstract

Many flat panel displays displays rely on polymeric substrates with thin film coatings, such as anti-reflective, anti-static and hardcoats, to improve optical and mechanical properties of the display. In this paper we briefly discuss the principles underlying the mechanical robustness of such coated structures, and examine two fitness-for-use tests currently employed by the industry. We compare the teachings with some results obtained with our hardcoats and anti-reflective coatings.

1 Objective and Background

The flat panel display industry applies varying types of thin coatings in order to achieve functionalities such as abrasion resistance (hard coats), anti-reflection (AR)[1-2] and static electricity dissipation or EMI shielding (anti-static)[3]. These coatings are applied on polymeric substrates on the outer surface of displays, and are therefore directly exposed to mechanical and chemical stress from the environment. As the trend towards more mobile and cost-effective displays continues, an increasing number of such coatings comprise organic crosslinked coatings, deposited via wet coating technology. Examples of this are hardcoated TAC films for polars, and AR- or AS-hardcoated PET for plasma applications.

This combination of relatively highly crosslinked thin coatings on deformable substrates presents challenges when considering mechanical robustness[4], especially in the area of single or double layer anti-reflective (AR) coatings, whose optical functionality requires thicknesses of ca 100nm. Mechanical durability of such submicron films is desired as any permanent deformation of the coating leads to local changes in the optical properties.

In order to evaluate the resistance to mechanical stress from the environment, the industry has established a number of mechanical fitness-for-use tests, such as pencil hardness and steel wool resistance. While widely applied, the mechanical principles underlying these tests and the effect of various material properties and coating structures on the outcome is less understood. In this paper, we aim to briefly investigate the underlying mechanical principles behind these tests and examine the role of the coating structure in relevant systems.

2. Mechanical models

2.1 Static indentation

During a pencil or steel wool test a load is applied to a coated substrate via the geometry of the indenter, resulting in a stress field in the coated substrate. This load can be static or dynamic (sliding), which adds a stress field originating from friction. We consider the case of both tests on a generic coated display film, i.e. a hardcoat of several micron thickness and one or two optical coatings of roughly 100nm thickness each. The adhesional strength of all interfaces is assumed to be strong. This situation is drawn schematically in Figures 1 and 2.

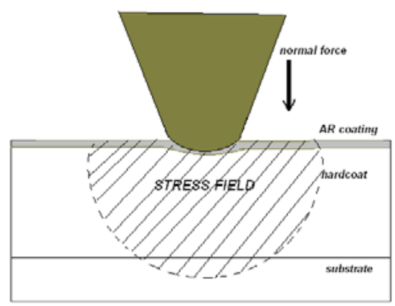

Figure !: schematic illustration of stress field in (static) pencil test

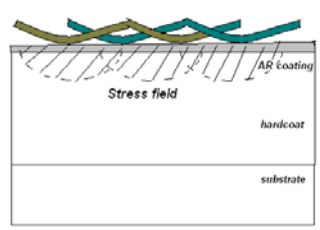

Figure 2: schematic illustration of stress field in steel wool test

In the case of the pencil test, the stress field in Figure 1 extends throughout the hardcoat, and interacts with the substrate. In the case of a steel wool test the stress field is more local, and acts solely on the optical coatings and the hardcoat.

The most simple explanation for this can be found considering Hertzian mechanics.[5,6] The ‘ dimension’ of a stress field of a static indenting load is given by

$$a = \left(\frac{3F(1-\nu^2)R}{4E} \right)^{1/3} \qquad (1)$$

where F is the force inserted on the indenter, R the (local spherical) bending curvature of the indenter, and $E/(1-\nu^2)$ the reduced modulus of the material. The highest static pressure that occurs in the material is given as

$$p_0 = \left(\frac{6F E^2}{\pi^3 R^2 (1-\nu^2)^2} \right)^{1/3} \quad (2)$$

Here the modulus of the indenter is considered much higher than that of the material, implying all elastic deformation occurs in the planar substrate. This is a reasonable assumption for a hard graphite pencil or steel thread indenting a polymeric film.

We now consider the pencil test and the steel wool test. In the pencil test a load of 750 gr is placed on a pencil tip, whose curvature of radius was observed to be 30 – 100 μm.[8] In the case of a hardcoat with reduced modulus 10 GPa (measured via nanoindentation) the stress field dimension is of the order of 4 - 7 micron. It is generally accepted that in the case of coating of thickness t the substrate does not contribute to the mechanical response upon indentation if $t > 2a$.[5,7] This indicates that in the pencil test the substrate will influence the outcome.

In contrast, the steel wool test the diameter of standard steel wool #0000 is 37 μm. A load of 250gr is applied to a swab of 1 $inch^2$. In the simplest approximation we assume that the load is evenly distributed over spherical contacts, resulting in a stress field of roughly 300nm and the highest pressure of the order 50 MPa. Evidently, in the actual test the stress is not distributed evenly as assumed here, but as the field scales with the normal force to the power 1/3, even a eightfold increase in load merely doubles the stress field. In all cases, it is clear that the depth of the field exerted by the steel wool is much smaller than the several micron hardcoat thickness.

We now consider the structure of a coated film. In the above it was shown that the stress field in the case of pencil tests extends into the substrate. This is undesirable, as the ability of hardcoats to resist strains is far less than that of the common polymeric films in use (PC, PET, TAC). This difference in resistance to strain leads to tensile flexural stresses at the hardcoat – substrate interface, which may induce failure of the coating.

In a paper of Gupta et al, the tensile flexural stresses were analysed as a function of the hardcoat / substrate modulus mismatch and the coating thickness.[7] The maximum flexural stress occuring in a coated substrate upon normal loading is reproduced in Figure 3 as a function of the ratio of layer thickness and stress field dimension, t/a, and modulus mismatch. Evidently, the bigger the mismatch, the higher the stress occurring from flexural strains. Also, a maximum in stress is observed if $t \cong a$.

Therefore, in the case of highly rigid hardcoats of several micron thickness on a relatively soft substrate, the flexural stresses may lead to brittle failure of the coating as a whole. Also, as hardcoat thicknesses of 4 – 8 are commonplace in the industry, the flexural stresses are maximal according to mechanical models. If the coating thickness increases beyond the range of the stress field, a, the tensural stress reduce. This results in an allowance for higher local stresses before failure, i.e. a higher pencil hardness.

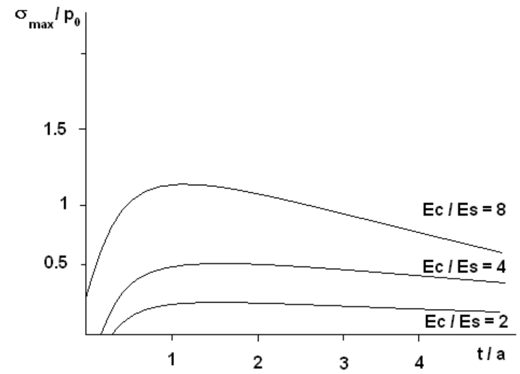

Figure 3: flexural stresses developed in a stacked system, for three ratios of moduli of the coating and substrate, from ref.7.

In the case of a very thin AR coating on a stiff hardcoat, the flexural stresses however are relatively small, as the modulus of crosslinked AR coatings is close or less than that of the hardcoat. Therefore, flexural stresses resulting from modulus mismatches are not a failure mode of AR coatings deposited on hardcoats.

2.2 Sliding friction

The above only considers static indentation, to which most coatings are rather resistant. In most mechanical tests however a dynamical movement is imposed on the indenter, thereby creating additional stresses due to friction. In this case, the most important contribution to failure is a shear stress occurring behind the indenter at the surface of the coating. In the most simple yet instructive model, the shear stress in the direction of sliding is given by

$$\sigma_x = -p_0 \left(\sqrt{1 - x^2 / a^2} + 2\mu x / a \right) \quad (3)$$

where μ is the coefficient of friction of the coating. and x is the distance from the contact center and all above assumptions are applied.[5] In Figure 4 we have plotted the tensile stress in the direction of sliding in the contact area for typical values encountered in a steel wool test for three values for the friction coefficient and two loads.

It is clear that a higher friction leads to higher tensile stress, especially at the edge of the contact. Within this simple analytical model, failure of the coating is predicted to be even more dependent on the coefficient of friction, i.e. the coating fails at a contact pressure

$$p_0 = \sigma_y / \mu \quad (4)$$

where σ_y is its yield strength. In a highly crosslinked coating this yield results in brittle cracks. An image of such brittle cracks in an antireflection coating - hardcoat combination is shown in Figure 5.

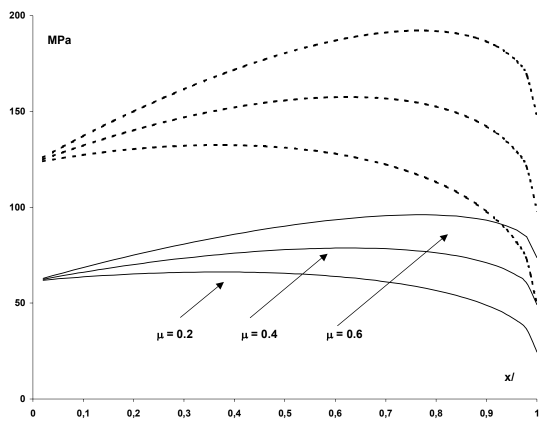

Figure 4; modeled surface contact stresses for 2 loads (250gr & 2kg) and three coefficients of friction in the steel wool test. Other parameters as in the text.

Using eq.(2), the critical force at which failure occurs scales as

$$F_{cri} \sim \left(\sigma_y / \mu\right)^3 \qquad (5)$$

It is thus clear that for the same yield stress of the coating material, a lower coefficient of friction results in a higher normal force upon yielding, i.e. the coating is more scratch resistance. Also, in the case of sliding with a relatively high coefficient of friction, the maximum in tensile stress is located at the surface, just behind the edge of the sliding indenter. This surface stress generally leads to surface failure, either that of the hardcoat or in the case of AR coating of the low refractive index topcoat.[9] It is thus clear that in order to minimize failure of optical coatings in the steel wool test the coefficient of friction of the upper coating needs to be low.

Figure 5: SEM images of OC-LR coating surface on hard coat after pencil hardness testing with 3H and 4H pencil.

3. Display coatings

PET and PC substrates were coated with an organic /inorganic hybrid hardcoat, 4D5-21 at various thicknesses. After evaporation of the solvent the hardcoat was cured with 1 J/cm^2 under nitrogen. The thickness was determined using a Lambda900 UV-vis spectrometer of Perkin-Elmer. The pencil hardness was tested using Mitsui pencils according to the JIS norm.[8] In Figure 6 we show the pencil hardness vs thickness for 4D5-21 on both substrates. It is clear that the hardness increases with increasing thickness. Yet the hardness of 4D5-21 on PC is significantly below that of PET, for equal thicknesses and curing conditions.

The underlying reason for this difference between PET and PC coated substrates is their modulus. PET is stiffer with a modulus of roughly 4 GPa vs 1.8 for PC. As presented in Figure 3, a stronger mismatch in modulus leads to higher flexural stresses, leading to failure in the pencil test.

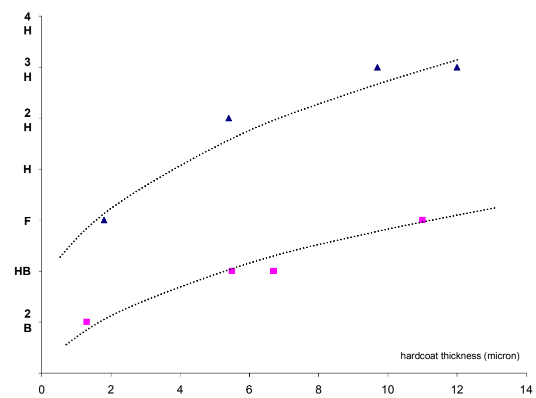

Figure 6; pencil hardness of hardcoat as a function of thickness using PET as substrate (diamonds) and PC (squares) accoring to the JIS norm. The lines are a guide to the eye.

In the case of AR coatings it was postulated that tensile stresses in the interface lead to failure. In order to investigate the importance of these sliding stresses, we measured the coefficient of friction of AR Optoclear™ coatings using a steel sled according to the ASTM method.[10] Also, the steel wool resistance was determined using 10 rubs of 250gr weight on 1 square inch 0000# steel wool. The grading goes from E (severely scratched) to C (~ 10-20 scratches) to A (no scratches) In Figure 7 we have plotted the steel wool test of our AR coatings as a function of the coefficient of friction of the coatings. As the coefficient of friction decreases, a significant improvement in the steel wool resistance of the coatings is observed. This improvement is due to the reduction of tensile stresses in the interface during the steel wool sliding.

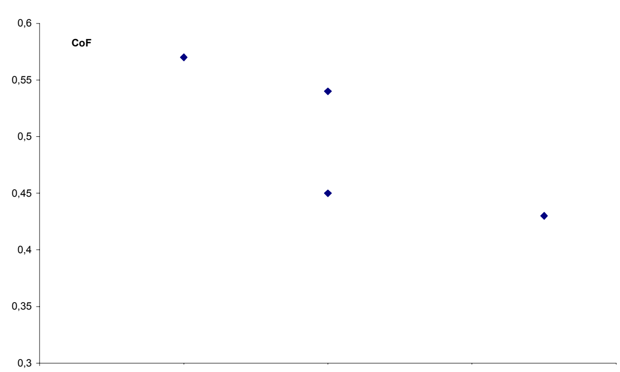

Figure 7 kinetic coefficient of friction of AR-HC coatings vs the steel wool performance..

4. Conclusions

In this paper we have briefly examined the mechanical principles underlying the robustness of display coatings in fit-for use tests. The pencil test is postulated to test the the robustness of the complete stack, whereas the steel wool test is relatively insensitive to the substrate and mostly predominantly tests the robustness of the AR coating.

In the case of micron thick hardcoats one of the most important features is the modulus mismatch between the hardcoat and substrate. A high mismatch leads to high flexural stresses, that induces failure in the pencil test. Therefore, the hardcoat must be optimised to the substrate.

In the case of AR coatings, tensile stresses occurring at the interface due to friction are believed to be the main cause of failure. Reducing these stresses via reducing the coefficient of friction leads to significant improvements of AR coatings in the steel wool test.

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